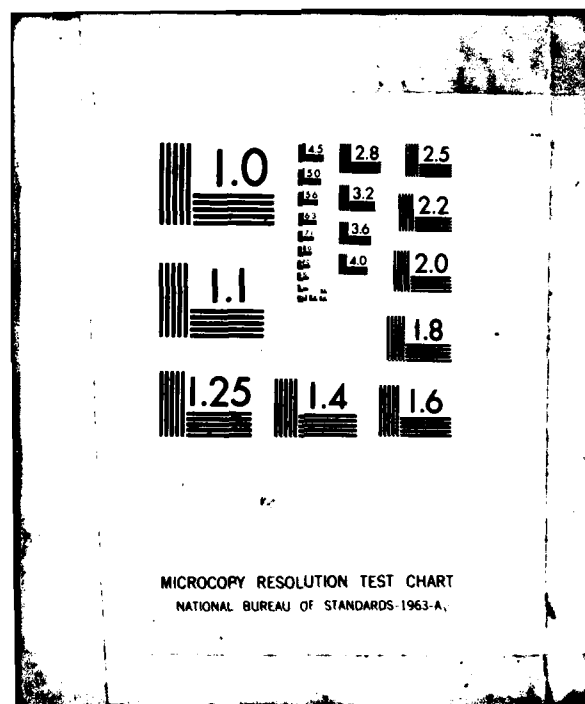


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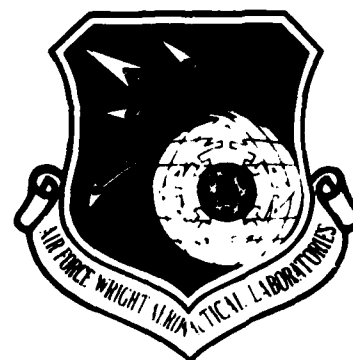
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TECHNIQUES SUITABLE FOR A PORTABLE WEAR METAL ANALYZER

THE PERKIN-ELMER CORPORATION
AEROSPACE DIVISION
2771 NORTH GAREY AVENUE
POMONA CA 91767

SEPTEMBER 1981

FINAL REPORT FOR PERIOD OCTOBER 1980 - APRIL 1981

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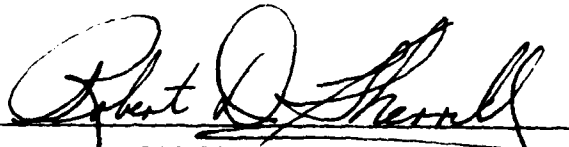


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this particular application. As a result, three optical techniques looked promising and their practicality was further investigated. The final assessment of these three techniques was based on the feasibility of making the instrument portable, low cost, able to analyze elements of interest, particle size independent, and with moderate power consumption. The three techniques, in order of suitability are: furnace atomic absorption spectroscopy, rotating disc electrode atomic emission spectroscopy, and DC plasma atomic emission spectroscopy.

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FOREWORD

This technical report was prepared by the Aerospace Division of the Perkin Elmer Corporation under Contract No F33615-80-C-2037. The work herein was accomplished under Project 3048, Task 304806, Work Unit No. 30480616, "Techniques Suitable for a Portable Wear Metal Analyzer", with Rebecca W. Newman, AFWAL/POSL as Project Engineer. The work was performed during the period 1 October 1980 to 30 April 1981. The report was released by the authors in September 1981.

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SUMMARY

Over three hundred articles including books, reports, journals, and commercial brochures were reviewed during this program. Based on this information, three suitable techniques are identified for the development of a portable wear metal analyzer. The techniques are ranked as follows:

- a. Furnace Atomic Absorption Spectroscopy. Furnace atomic absorption spectrometers are relatively low cost and particle-size independent. No sample pretreatment is required and the results can be correlated with the data from the Air Force laboratories. Instruments can be made portable and are easy to set up and operate.
- b. Rotating Disc Atomic Emission Spectroscopy. Rotating disc atomic emission spectrometers are widely used in Air Force laboratories. Instruments are easy to operate, provide rapid analysis and require no sample treatment. However, the present instrument weighs 500 pounds and the high resolution requirement for the spectrometer would make a portable design difficult to achieve.
- c. DC Plasma Atomic Emission Spectroscopy. DC plasma atomic emission spectrometers have recently been introduced to Air Force laboratories. They are versatile multielement instruments which could be made smaller than present commercial products. However, the high consumption of argon gas, making replenishment difficult, and the relatively high cost of the instrument are disadvantages.

TABLE OF CONTENTS

	<u>Page</u>
REPORT DOCUMENTATION PAGE	ii
SUMMARY	iv
1. INTRODUCTION	1
1.1 Wear Metal Analysis	1
1.2 Joint Oil Analysis Program	1
1.3 Operational Need	2
1.4 Scope of the Feasibility Study	3
2. APPROACH	4
2.1 Literature Search	4
2.2 Data Reduction	4
2.3 Fundamental Principles Investigation	4
2.4 "Must" Criteria Screening	4
2.5 Practical Instrument Consideration	5
2.6 Rating	5
2.7 References	5
3. MANDATORY CRITERIA SCREENING	6
3.1 Evaluation Criteria	6
3.2 General Comparison	8
3.3 Screening	9
4. FIELD INSTRUMENT CONSIDERATIONS	15
4.1 Detection Systems	15
4.2 Data Reduction System	16
4.3 Rotating Disc Electrode Atomic Emission Spectroscopy	16
4.4 DC Plasma Atomic Emission Spectroscopy	18
4.5 Furnace Atomic Absorption Spectroscopy	18
4.6 Portable Instrument Configuration	22
5. PERFORMANCE PARAMETERS	23
5.1 Matrix Effect	23
5.2 Spectral Interference	23
5.3 Particle Settling Rates	24
5.4 Particle Size and Atomization	24
6. RATING OF TECHNIQUES	26
6.1 Rating Criteria	26
6.2 Rating	27

TABLE OF CONTENTS (Concluded)

	<u>Page</u>
7. CONCLUSION	29
LIST OF REFERENCES	30
BIBLIOGRAPHY	32
APPENDIX A - FUNDAMENTAL PRINCIPLES OF INSTRUMENTAL TECHNIQUES	45
APPENDIX B - DATA MATRICES	58
APPENDIX C - RADIATION LEVEL CALCULATION FOR RADIOACTIVE TAGGING TECHNIQUES	69
APPENDIX D - GENERAL COMPARISON OF THE TEN TECHNIQUES	71
APPENDIX E - EVALUATION OF PRECONCENTRATION OF WEAR METALS FOR X-RAY FLUORESCENCE ANALYSIS: FILTER CLOGGING	72
APPENDIX F - BASIC LIMITING FACTORS TO FACILITATE A SIZE EVALUATION FOR OPTICAL SPECTROMETERS	73
APPENDIX G - THEORETICAL DETERMINATION OF SETTLING RATES VERSUS PARTICLE SIZE AND VISCOSITY OF OIL	76
APPENDIX H - EFFECT OF PARTICLE SIZE ON PARTS PER MILLION (PPM) LIMITS AND PRECISION IN FURNACE ATOMIC ABSORPTION SPECTROSCOPY	78
LIST OF ABBREVIATIONS, ACRONYMS AND SYMBOLS	80

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Instrument Parameters for Rotating Disc Electrode Atomic Emission Spectroscopy	17
2	Instrument Parameters for DC Plasma Atomic Emission Spectroscopy	19
3	Instrumental Parameters for Furnace Atomic Absorption Spectroscopy	20
A-1	Atomic Model	46
A-2	Schematic Diagrams for (I) Atomic Emission (II) Atomic Absorption (III) Wavelength-Dispersive X-Ray Fluorescence (IV) Energy-Dispersive X-Ray Fluorescence	48
A-3	Schematic Diagram for a Colorimetric Configuration	57

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Detection Limits in Parts Per Million (PPM)	8
2	Evaluation and Summary of the Ten Techniques	10
3	Comparison Table of Top Three Techniques	28
B-1	Data Matrix	58
G-1	Settling Rate in Millimeters per Minute for Various Particle Sizes at 1, 10, 100 and 1000 Centipoise Oil Viscosity	77
H-1	Concentration (PPM) for One Particle in 20 Microliter Sample as a Function of Particle Size	78

1. INTRODUCTION

1.1 WEAR METAL ANALYSIS. The analysis of wear metals in oil is a testing technique to monitor the internal condition of fluid-lubricated mechanical systems. Wear metal particles are generated by the relative motion between the contact area of metallic parts. The metal particles then enter the surrounding lubricant. When equipment is operating normally, the wear metals are produced at a constant rate. An abnormal wear rate can be related to the probable source within the equipment and appropriate maintenance action can be taken before failure occurs.

1.2 JOINT OIL ANALYSIS PROGRAM. The Joint Oil Analysis Program (JOAP) is a preventive maintenance procedure for engines and transmissions. The procedure involves analysis of an oil sample by atomic emission or atomic absorption spectroscopy. Spectrometric oil analysis, often referred to as Spectroscopic Oil Analysis Program (SOAP), was first initiated by the railroad industry for diesel locomotives. Application to military aircraft began with the U.S. Navy in 1955 (NOAP). Subsequently, the Army joined the oil analysis in 1959 (ASOAP). The Air Force established an oil analysis program in 1962, and by 1967 the Joint Oil Analysis Program (JOAP) was implemented.

1.2.1 Common Sources of Wear. Iron is the major metal used in bearings, cylinder walls and piston rings and is the dominant wear metal found in lubricating oil. In a 1972 report, iron appeared as an indicator in approximately 86% of all failures detected by wear metal analysis.¹ Silver plating is used in bearing cages, gear teeth and shafts, while titanium is employed in bearing hubs. These three elements have been identified as having the highest priority for measurement by any portable wear metal analyzer.

1.2.2 Effectiveness of JOAP. The Air Force reported in 1971² that with the use of the oil analysis program for detecting abnormal-wear-before-failure occurrences, a success rate of over 95% was achieved. In 1973, their fixed-wing aircraft engine program had a success rate of 96%. The Air Force fiscal year 1976 program also had a success rate of 96% which resulted in a net savings of 59 million dollars. Presently, the Air Force has over 100 SOAP laboratories throughout the world, and over 1.5 million samples are analyzed yearly.

1.2.3 Limitations. The spectrometric fluid analysis method is effective only for those failures which are characterized by an abnormal increase in the wear metal content of the lubricating fluid.³

1. Bond, B.B., "Wear Metal Analysis of Lubricating Oils", Development in Applied Spectroscopy, 10, (1972), p. 285
2. Beerbower, A., "Mechanical Failure Prognosis Through Oil Debris Monitoring", Contract No. DAAJ02-73-C-0005 Report
3. "Joint Oil Analysis Program Laboratory Manual", Navy 17-15-50 Navair, Army TM38-301, Air Force T.O. 33-1-37, (1978)

Failures must proceed at a rate slow enough to permit corrective action to be taken by the operating personnel after receipt of adverse notice from the laboratory. Examples of both detectable and undetectable failures are listed below.

a. Routine Detectable Failures.

1. Damaged cylinders in reciprocating engines. Such damage includes worn or broken piston rings and bands, scored or scuffed pistons and cylinder walls, damaged piston pins, broken valve springs and loose or defective valve guides.
2. Worn, misaligned or broken anti-friction bearings and retainers.
3. Worn, misaligned or scored gears.
4. Worn or scored journal bearing surfaces.
5. Cracked or broken reciprocating engine master rod bearing shells and splines.
6. Slow progressive failures which add to the wear metals content of the fluid system, either directly by relative motion between mating surfaces or indirectly by misalignment of mating surfaces.

b. Failures Which Cannot be Detected by Spectrometric Analysis.

1. Spectrometers will not detect chips or wear metal particles that are visible to the eye.
2. Failures which occur too rapidly to be detected by fluid analysis including failures due to fluid starvation and bearing seizure.
3. Failures of major assemblies which proceed from the start of the failure to total failure without a significant production of wear metals. This category includes most fatigue failures. To date, progressive fatigue damage cannot be detected.

1.3 OPERATIONAL NEED. When combat and reconnaissance aircraft are deployed away from their home bases, the requirement for engine oil analysis still exists. The requirement to analyze aircraft engine oil on an "after each flight" basis is due to the critical nature of aircraft turbine engines and to the potential danger of failure to accomplish a given mission.⁴ Because more complex engines are coming into use, it is vital that a compact, easy-to-operate, and highly reliable system be developed to analyze engine oil during aircraft deployments. Rapid instrumental setup to accomplish post-deployment analysis prior to the first mission is desirable. Simplicity of

4. USAF, "Statement of Operational Need for a Lightweight Portable Aircraft Engine Oil Analysis Unit," TAF 305-80, 15 May 1980

operation and speed of analysis are required to accomplish the workload associated with the high sample-generation rates resulting from quick turn-around operations. The instrument must be capable of rapid analysis of the common wear metals associated with current aircraft engines and gearboxes. The capability to increase the number of wear metals analyzed is highly desirable. When deployed, the unit should be able to operate with a minimum amount of expendable materials and be capable of operating from 110 or 220V/50 or 60 Hertz (Hz). The need for sustained operation without the resupply of expendable materials is essential in a combat scenario; however, expendables make up much of the volume and weight of the presently deployable spectrometer. The ideal deployable oil analysis instrument would be self-contained and include the calibration standards needed in actual use. The unit should be designed to meet current Air Force design criteria.

1.4 SCOPE OF THE FEASIBILITY STUDY. The present program is a literature study to identify the optimum technique suitable for developing a portable wear metal analyzer.

1.4.1 Prospective Techniques. Ten techniques have been evaluated for their suitability:

- a. Atomic emission spectroscopy - with rotating disc electrode, graphite furnace, and plasma flame as sample atomization and excitation source.
- b. Atomic absorption spectroscopy - with chemical flame, graphite furnace, and plasma flame as sample atomization source.
- c. X-ray fluorescence spectroscopy - with energy-dispersive and wavelength-dispersive detection.
- d. Colorimetry.
- e. Radioactive tagging.

1.4.2 Suitability. The four most important criteria for the suitability of the above ten techniques were as follows:

- a. Portability.
- b. Manufacturing costs.
- c. Multielement capability.
- d. Wear metal particle-size dependency.

Also addressed were the accuracy expected for the various techniques and the influence on the accuracy of the technique by the presence of other elements or of different oil base stocks. The electrical requirements needed for each technique and how these requirements affect the portability of the instrument under consideration were also determined. Finally, such practical criteria as time of analysis, safety, ruggedness and durability, ease of operation, low cost per analysis, minimal use of consumables and support equipment, and size of sample were considered.

2. APPROACH

The study proceeded through the following sequence of activities:

- a. Literature search.
- b. Data reduction.
- c. Fundamental principles investigation.
- d. Mandatory criteria screening.
- e. Practical instrument considerations.
- f. Rating.

2.1 LITERATURE SEARCH. A literature study of the state-of-the-art for the feasibility of developing a portable wear metal analyzer focused on extracting information from the existing literature and commercial brochures. Since most of the literature related to the analysis of metals in oil is covered by Chemical Abstracts, a computer search using the Chemical Abstracts data base was conducted. The first task was to compile a set of key words related to the Statement of Work. These words were grouped into different categories: Oil, elements of interest, analytical techniques, and technique-associated parameters. They were then combined into different combinations in order to eliminate most of the irrelevant information. Other data base searches, such as National Aeronautics and Space Administration (NASA) and Department of Defense (DOD), have also been conducted. Two published searches on "Lubricating Oil Analysis for Wear Monitoring" by the National Technical Information Service (NTIS) were used extensively. The annual review in the April issue of Analytical Chemistry was also a major source of information. Thirty instrument manufacturers associated with the specified techniques were solicited for information; fifteen of them replied providing a significant amount of practical data.

2.2 DATA REDUCTION. Information in the literature pertinent to the portable wear metal analyzer was compiled into tables for comparison (Appendix B). Each chart describes one of the ten techniques under consideration. These tables show the capability of each technique as indicated by existing commercially available instruments.

2.3 FUNDAMENTAL PRINCIPLES INVESTIGATION. The feasibility study evaluation involved two steps. The first step was to determine whether there were any fundamental limitations while the second step investigated the practical considerations. Therefore, the fundamental principles for each of the techniques are discussed in Appendix A while the practical considerations are noted in Section 4.

2.4 "MUST" CRITERIA SCREENING. It was impractical to equally consider in detail all ten of the prospective techniques. An initial screening was therefore employed to eliminate some of the less feasible approaches. A set of parameters was generated relative to the portable wear metal analyzer and based on

the suitability criteria indicated in Paragraph 1.4.2. These parameters were grouped into "musts" and "goals" and each of the ten techniques was screened according to these "musts" criteria. The results of this screening are discussed in detail in Section 3. Only three of the ten techniques survived this screening of "musts" criteria.

2.5 PRACTICAL INSTRUMENT CONSIDERATION. After the "musts" criteria screening had been completed, the instrumental parameters for the remaining techniques were considered. Although no attempt was made to design a final instrument, some practical considerations are discussed in block diagram form in Section 4. Most techniques involved are somewhat affected by interference, sample matrix, particle size and other parameters, which are discussed in Section 5.

2.6 RATING. Finally, the remaining three techniques that passed the initial screening were rated according to the priority criteria specified by the Air Force. These criteria are portability, cost, multielement capability and particle-size independence.

2.7 REFERENCES. Due to the large amount of information involved, only the most pertinent literature is included and these references are grouped according to the topics in the bibliography. Titles of the articles are listed so as to indicate the subject matter of the article. Therefore, for simplicity, only the references affecting the evaluation are cited in the text.

3. MANDATORY CRITERIA SCREENING

3.1 EVALUATION CRITERIA. In the screening process, the emphasis was placed on the fundamental limitations of the technique, which prevent it from being useful as a portable wear metal analyzer. Practical limitations which might be alleviated by suitable instrumental design were not used as the criteria for rejecting certain techniques. Therefore, if a technique failed to meet one of the mandatory criteria, the technique was rejected.

3.1.1 "Musts". The following "musts" criteria were considered as mandatory to the portable wear metal analyzer. They were developed according to Air Force direction and our understanding of the problem.

- a. Multielement Capability. The instrument must be capable of analyzing the following elements over the indicated ranges:

<u>Element</u>	<u>Range in Parts Per Million (PPM)</u>
Fe	0-125
Ti	0-16
Ag	0-10
Al	0-40
Ni	0-10

These ranges would allow the instrument to monitor up to the highest abnormal wear levels encountered for all engines, transmissions, and other mechanical devices covered in the JOAP program.⁵

- b. Acceptable Performance. The instrument must not only have acceptable lower detection limits and precision in order to detect the early wear of engine parts, but also good repeatability at these levels, so that abnormal trends are readily apparent.

The necessary lower detection limits and precision have been determined from the JOAP Program Laboratory Manual, Reference 5. For every engine, transmission, and gear box specified, a parts per million concentration level is given which indicates an abnormal trend in a 10 hour period. The acceptable instrument should be capable of measuring 1/10 of the smallest listed abnormal trend. For the five mandatory elements, this minimum figure then becomes:

<u>Element</u>	<u>Minimum Detection Level (PPM)</u>
Fe	0.3
Ti	0.2
Ag	0.2
Al	0.2
Ni	0.3

5. "Joint Oil Analysis Program Laboratory Manual", Navy 17-15-50 Navair, Army TM 38-301, Air Force T.O. 33-1-37, (1978)

- c. Portability. The instrument must be designed as a one-person portable package. The package may be one or two suitcases. The weight limits for one-person portability are contained in applicable military specifications and standards, such as MIL-STD-1472. In this standard, the limit for one suitcase-type package is 35 pounds, providing that the package is balanced. In any case, the practical limit for a one-person portable instrument is around 80 pounds.
- d. Rapid Analysis. The total cycle time for an analysis must be such that a complete analysis may be performed in 10 minutes, preferably in 5 minutes. The present technique utilized in base JOAP laboratories, the rotating disc atomic emission technique, can perform 50 to 60 analyses per hour once the equipment is set up and running. A portable unit must be capable of performing a minimum of six analyses, and preferably, twelve analyses per hour, in order to avoid limiting the turnaround rate of operational aircraft.
- e. Safety. The technique must not jeopardize personnel safety during transportation, operation, maintenance and supply support. Current field units, using the flame atomic absorption technique, jeopardize personnel safety during operation (proper flame setup to prevent explosion) and during supply support (supply of nitrous oxide (N_2O), acetylene (C_2H_2) and methyl-isobutyl ketone (MIBK)).

3.1.2 Goals. After the initial screening for "musts" criteria, the remaining techniques were screened for suitability using the following additional criteria:

- a. Ability to measure chromium, silicon, magnesium and copper with adequate sensitivity in addition to the five "must" elements.
- b. Particle-size independence.
- c. Repeatability of measurements.
- d. Use of existing JOAP Conostan standards.
- e. Viscosity independence.
- f. Suitability for various power sources.
- g. Requirement for minimum consumables.
- h. Low initial cost and operating cost.
- i. Simplicity of sample preparation.
- j. Requirement for low power.
- k. Potential for rugged construction for field use.

3.2 GENERAL COMPARISON. One of the basic requirements of the portable wear metal analyzer is to adequately determine elements of low concentration. Thus the elements of interest versus detection limit, precision, and repeatability, are compiled into data matrices. These matrices are shown in Appendix B and each matrix describes one of the ten techniques studied. The radioactive tagging technique is somewhat different in nature and therefore is treated separately throughout the text in Appendix A and, more specifically, in Appendix C, which concerns safety. A summary of the data matrices is given in Table 1, showing the detection limits of the techniques.

TABLE 1. DETECTION LIMITS IN PARTS PER MILLION (PPM)

	Fe	Ti	Ag	Al	Ni
"Must" Criteria (Mandatory Detect- able Level)	0.3	0.2	0.2	0.2	0.3
Flame Atomic Absorption Spectroscopy	0.004	0.1	0.001	0.1	0.005
Plasma Atomic Absorption Spectroscopy	2.0	5.0	0.5	N/A*	2.0
Graphite Furnace Atomic Absorp- tion Spectroscopy	5×10^{-5}	2×10^{-3}	5×10^{-6}	5×10^{-5}	4.5×10^{-4}
Rotary Disc Atomic Emission Spectroscopy	0.2	0.1	0.002	0.1	0.3
Graphite Furnace Atomic Emission Spectroscopy	0.017	0.01	4×10^{-4}	4×10^{-5}	4×10^{-3}
Plasma Atomic ICP** Emission Spec- troscopy	0.04	0.03	0.02	0.09	0.1
DCP***	0.02	0.026	0.026	0.032	0.08
Energy Dispersive X-Ray Fluorescence Spectroscopy	0.7	1.0	1.0	> 10	0.7
Wavelength Dis- persive X-Ray Fluorescence Spectroscopy	2	8	5	3	4
Colorimetry	0.03	0.01	0.01	0.1	0.1
Radioactive Tagging	NOT TABULATED				

* N/A = not available

** ICP = inductively coupled plasma

*** DCP = direct current plasma

3.3 SCREENING. The techniques were evaluated according to the "musts" criteria. As mentioned earlier, if a technique fails to meet one of the "musts" criteria, the technique was rejected. All of the referenced documents played a part in this evaluation. If no commercially available product could meet the performance requirements in a laboratory, then a ruggedized miniature unit would be even less likely to do so. If the technique is not regularly used in a laboratory instrument and if very few papers have been written about the technique; then the technique is not likely to be suitable for a portable instrument. Although some of the techniques that meet the performance requirements are available in suitably portable form, allowance was given to the possibility that miniaturization and modern packaging could overcome this deficit. The safety criteria is necessarily subjective; however, the necessity of handling flammable pressurized gases or very strong acids, even in prepackaged form, was considered undesirable for this application. The results of the screening are tabulated in Table 2 and presented in more detail below. Refer to Appendix A for detailed discussion of the fundamental approach of each technique. A general comparison of the techniques is shown in Appendix D.

3.3.1 Rejected Techniques

- a. Atomic Absorption Spectroscopy with a Flame Source. Although this technique has been used in many SOAP laboratories, the need for using N_2O and C_2H_2 makes it undesirable. The explosive nature of these gases may be hazardous to the operator or personnel transporting the gas supplies. Therefore, this technique failed the safety criterion. In addition, although the basic instrument is capable of being packaged in a relatively lightweight form; the auxiliary equipment, such as pressure gauges, valves, bottled gases, test tubes, and with a flame source solvent for sample dilution means that an instrument using the atomic absorption spectroscopic technique cannot be made portable.
 - b. Atomic Absorption Spectroscopy with a Plasma Source. The use of a radio frequency (RF) or direct current (DC) plasma as the atomizer for atomic absorption was introduced, mainly in research laboratories, prior to 1969. Advantages are that the higher temperature of the plasma discharge improves the atomization efficiency and the operation of the plasma in an inert gas environment reduces the effects of compound formation. However, it was found that sometimes the emission signal of the element was stronger than that of the hollow cathode source and the former caused interference. The noise produced by the emission signal also imposed a limit on detectability. Also, the reported detection limit for aluminum was 30 ppm⁶, which is not acceptable. Therefore, this technique was rejected for unacceptable performance.
 - c. Atomic Emission Spectroscopy with a Graphite Furnace. In a graphite furnace, the atomization process occurs in the time frame of a few hundred milliseconds to a second and is very efficient. However, the maximum temperature that can be reached by a graphite furnace (approximately 3000°C) is relatively low compared to plasma and spark sources. The relatively low atomization/excitation temperature causes
6. Veillon, C., M. Margoshes, "An Evaluation of the Inductively-Coupled Radio Frequency Plasma Torch for Atomic Emission and Atomic Absorption Spectroscopy", Spectrochimica, Acta, 23B, (1968), p. 503

TABLE 2. Evaluation and Summary of the Ten Techniques

Technique	Analysis of 5 Elements	Acceptable Performance	Portability	Fast Analysis	Safety	Fail/Pass	Reasons for "FAIL"
Flame Atomic Absorption	Yes	Yes	No	Yes	No	FAIL	The use and transport of N_2O and C_2H_2 may be hazardous. The weight of two gas cylinders is prohibitive.
Plasma Atomic Absorption	Yes	No	Difficult	Yes	Yes	FAIL	Lack of sensitivity. Emission effect causes interference. Little work done in this area. ICP source can not be made portable.
Graphite Furnace Atomic Absorption	Yes	Yes	Yes	Yes	Yes	PASS	
Rot. Disc Electrode Atomic Emission	Yes	Yes	Difficult	Yes	Yes	PASS	
Graphite Furnace Atomic Emission	Yes	No	Difficult	Yes	Yes	FAIL	Self absorption and self reversal of emission signal within the graphite tube results in poor linearity. Graphite is not a very efficient emission source. Little work done in this area.
Plasma Atomic Emission	Yes	Yes	ICP-No DCP-Difficult	Yes	Yes	ICP-FAIL DCP-PASS	The bulky RF generator used in ICP makes it not possible to be made portable.
Energy Dispersive X-ray Fluorescence	Yes	No	Yes	Difficult	Yes	FAIL	Sensitivity is insufficient to detect the full range of the five "must" elements.
Wavelength Dispersive X-ray Fluorescence	Yes	No	Yes	Difficult	Yes	FAIL	Sensitivity is insufficient to detect the full range of the five "must" elements.
Colorimetry	Yes	Yes	Yes	No	No	FAIL	Reaction time is slow. The use and transport of hydrofluoric acid-Agus Regia may be hazardous
Radioactive Tagging	No	No	Yes	Yes	No	FAIL	Do not have adequate half-life for all five "must" elements. Radiation hazard.

the presence of a large number of ground state atoms, which, coupled with a relatively long optical path length, causes self-absorption; the latter effect, in turn, can lead to nonlinearity of the emission signal versus concentration.⁷ The incandescent graphite tube emits a strong continuum, which causes a background problem. These limitations make the technique undesirable for general laboratory use and unacceptable for the portable wear metal analyzer application.

- d. Colorimetric Method. The basic procedure for colorimetric analysis includes the following: acid extraction of the metals, adjustment of pH with buffer solutions, addition of reagent for color development and colorimetric measurement. Although an adequate instrumental design could automate all the wet chemical procedures, the overall time involved is relatively long.⁸ A postulated automatic system with parallel, simultaneous processing is shown in Appendix A. Despite the automation shown, the system would limit the user to four analyses per hour. This limitation would severely handicap the flight squadron during the sortie surge operations workload. Therefore, the technique was rejected because of the analysis time required.

The acids required include hydrofluoric acid (HF), hydrochloric acid (HCl) and nitric acid (HNO₃). The transportation, handling, and disposal of these acids may be hazardous. Although the acids may be prepackaged so that a transporter or an operator need not handle them, the very presence of such hazardous materials provides opportunity for accident.

- e. Radioactive Tagging. Most of the work on radioactive tagging described in the literature had been done with automotive engines prior to 1970.⁹ The use of the radioactive tagging technique for the portable wear metal analyzer presents two problems: first, isotopes with adequate half-life for all five required elements do not exist; second, the radiation level resulting from the radioactivity of the irradiated part is too high for the safety requirement of the maintenance personnel. Calculations for an assumed case are shown in Appendix C. Therefore, radioactive tagging fails both performance and safety criteria.
- f. X-Ray Fluorescence Spectroscopy (XRFS) (Energy Dispersive). The best feature of the energy-dispersive XRFS technique is that the technique can be made portable. Instruments of less than 30 pounds are available commercially. Unfortunately, the sensitivity is limited and cannot meet the required minimum detection limits. However, due to the desirable feature of portability, the XRFS method has been extensively investigated and the rationale for rejection is discussed in greater detail in Section 3.3.2.

7. Epstein, M.S., T.C. Rains, T.J. Brady, J.R. Moody, I.L. Barnes, "Determination of Several Trade Metals in Simulated Fresh Water by Graphite Furnace Atomic Emission Spectroscopy", Analytical Chemistry, 50:7, (1978), p. 874
8. Sandell, E.P., "Colorimetric Determination of Trace Metals", Wiley, NY. (1978), 4th Edition
9. Brugger, J.E., F.F. Rieke, R.A. Semmler, "Engine--Wear Studies With Radioisotopes", Isotopes And Radiation Technology, 1:3, (1964), p. 256

- g. X-Ray Fluorescence Spectroscopy (Wavelength-Dispersive). The wavelength-dispersive method is also not able to meet the required minimum detection limits. Compared to the energy-dispersive method, the single element detectability for both methods is about the same. The wavelength-dispersive method is better for lighter elements and the energy-dispersive method is better for heavier elements. Wavelength-dispersive spectrometers have a much better resolution but a smaller angle of acceptance so that a greater source (less portable) is needed. A multiple crystal spectrometer can analyze five elements simultaneously with a shorter counting time, but the setup is more critical. There is no obvious advantage in using the wavelength-dispersive XRFS method as compared to the energy-dispersive XRFS method. Therefore, both X-ray techniques are rejected.

3.3.2 The XRFS Method

- a. The capability for detecting elements of low atomic number at low concentrations is limited due to the following:
1. Because the energy of an electron in the shell of quantum number, n , is proportional to the square of the atomic number, Z , the characteristic radiations for the low Z elements have relatively long wavelengths (low energy). The low energy X-ray is easily attenuated by the window of the X-ray tube, and the characteristic radiation from the sample is further absorbed by the detector window.
 2. The low energy radiation results in a small depth of penetration of the sample.
 3. Because the Auger effect predominates below the atomic number 20, the yield of fluorescent X-rays from the sample drops off rapidly.¹⁰
 4. For wavelength-dispersive XRFS, an efficient analyzing crystal with appropriate lattice spacing to match the wavelengths for low Z elements is not available.
 5. For energy-dispersive XRFS, the resolution is poorer for low Z elements because the width of the pulse-height distribution for a detector is proportional to the square root of the energy of an X-ray photon.¹¹
- b. The major factor limiting the detectability of XRFS is the continuum background presented in the X-ray tube. One way to improve the detection limit is to use a secondary target, which is excited from the radiation of an X-ray tube. The X-ray produced by the secondary

10. Birks, L.S., "X-Ray Spectrochemical Analysis", Interscience, N.Y., (1959)

11. Jenkins, R., J.L. DeVries, "Practical X-Ray Spectrometry", Springer-Verlag, N.Y., (1973)

target is essentially a simple line structure from the target element. The unwanted continuum background is therefore greatly reduced. However, the production of X-rays is a very inefficient process, and the use of secondary targets was found to be practical only recently with advances of X-ray tube technology. Even with use of secondary targets, the required minimum detection limits still cannot be met.¹²

- c. By placing a foil or film of chosen material between the tube and the sample, some of the undesirable continuum can be removed. This method can be used selectively to improve the minimum detection limit.^{13,14} By using this method together with the secondary targets, the state-of-the-art laboratory instrument can measure down to the ppm region for elements with $Z > 20$. However, it does not appear possible to miniaturize these laboratory instruments into a portable field instrument and retain this sensitivity.
- d. Polarized X-rays can be used to improve the signal-to-background ratio obtained in a given measurement. Light elements, such as carbon or boron carbide, can be used as polarizers. The paths between the source, polarizer, sample, and detector are mutually orthogonal.^{15,16} This arrangement reduces the scattering from sample to detector. However, the reduction of background may be accompanied by a decrease in the count rate. Published works in this area are mostly in research laboratories, and their practical applications to the portable wear metal analyzer is unknown.
- e. Laboratory instruments use liquid nitrogen-cooled silicon (Si)-lithium (Li) detectors. For field instruments, one needs to use a proportional counter which results in a minimum detection limit approximately three times poorer than for a Si (Li) detector.¹⁷
- f. The filtration method can be used to preconcentrate the sample.¹⁸ However, the difficulties encountered are as follows:

- 12. Kevex Corporation, 1101 Chess Drive, P.O. Box 4050, Foster City, CA 94404
- 13. Ibid.
- 14. United Scientific Corporation, 1400 D. Stierlin Rd., P.O. Box 1389, Mountain View, CA 94042
- 15. Dzubay, T.G., B.V. Jarrett, J.M. Jaklevic, "Background Reduction in X-ray Fluorescence Spectra Using Polarization", Nuclear Instruments and Methods, 115, (1974), p. 297
- 16. Ryon, R.W., J.D. Zahct, "Improved X-Ray Fluorescence Capabilities by Excitation With High Intensity Polarized X-Rays", Advances in X-Ray Analysis, 22, (1979), p. 453
- 17. Bertin, E.P., "Introduction to X-Ray Spectrometer Analysis", Plenum Press, N.Y., (1978)
- 18. Ruff, A.W., "Characterization of Debris Particles Recovered from Wearing Systems", Wear, 42, (1977), p. 49

1. The smallest filter that can be used has approximately a 0.1 micron pore size; yet a large portion of the wear metal is of a size between 0.01 micron to 0.1 micron,¹⁹ as well as dissolved metal.
2. The particle-size distribution varies with the type of wear.
3. Conostan standards cannot be used, since these are organometallic solutions that would pass through the filter.
4. The results cannot correlate with base laboratory measurements because implementation of new standards would be necessary.
5. The filter may be subject to clogging (see Appendix D).
6. Filtering of the sample would complicate the operation, and affect accuracy and precision.

3.3.3 Selections. The reasons for selecting the promising techniques are also discussed below.

- a. Atomic Emission Spectroscopy (AES) with a Rotating Disc Electrode. The rotating disc atomic emission technique has been used for SOAP for many years.²⁰ It is a fast multielement technique, and does not need sample preparation or inert gas purging. Therefore, it is considered as a promising method.
- b. Atomic Emission Spectroscopy with a DC Plasma Flame. DC plasma atomic emission has been used recently in some Air Force laboratories for research programs in oil analysis.²¹ The use of an Echelle Spectrometer makes it relatively lightweight compared to other AES instruments.
- c. Atomic Absorption Spectroscopy (AAS) with a Graphite Furnace. There is no commercial instrument available for the multielement analysis using furnace atomic absorption technique. However, by using a multielement lamp(s) and a polychromator, a furnace atomic absorption spectrometer can be made portable with multielement capability.²²

19. Johari, O., I. Corvin, A.V. Samudra, J. Staschke, "Four Men's Point of View - A Joint Paper on the Correlation of Spectrographic Oil Analysis Data with Scanning Electron Microscopy and X-ray Data on Particles in Hydraulic Oils", Industrial Lubrication and Tribology, 31, (1979), p. 172
20. JOAP Manual (1978)
21. Spectrametrics, Inc., 204 Andover Street, Andover, MA 01810
22. Harnly, J.M., T.C. O'Haver, B. Golden, W.R. Wolf, "Background Corrected Simultaneous Multielement Atomic Absorption Spectrometer", Analytical Chemistry, 51:12, (1979), p. 2007

4. FIELD INSTRUMENT CONSIDERATIONS

The instrumental parameters for the three techniques that passed the "musts" criteria are considered in this section. Since they are all optical spectroscopic methods, some of the subsystems that are common to all three techniques (such as a detection system and data reduction system) are discussed first. The subsystems which are unique to each individual technique will be discussed subsequently.

4.1 DETECTION SYSTEMS

4.1.1 Wavelength Selection Element

- a. Filter. The filter is the simplest monochromating device. It has the further advantage of being extremely rugged. However, the best filter now available has a spectral bandpass of about 50 Angstroms (\AA) and cannot be used for either AES or AAS instruments.
- b. Prism. The refractive index of a prism varies with wavelength and is the basis for using a prism as a dispersion element. Prisms have not been used extensively in modern optical spectroscopy primarily because of the difficulty associated with construction of large aperture prism instruments.
- c. Grating. The diffraction grating is used in most of the optical spectrometers and utilizes the principle of light interference to display a spectrum as a function of the angle at which light is reflected from the grating surface. In general, the grating is superior to the prism and the filter.

4.1.2 Sequential Detection Mode

- a. Scanning. Only one photomultiplier detector is used and the grating is mechanically rotated so that the whole spectral range is covered.
- b. Image Dissector. In the image dissector photomultiplier, a slit aperture plate is placed between a photocathode and the first dynode. Light image incident on the photocathode forms an electron image on the aperture plate. This electron image is swept across the face of the plate by electromagnetic sweep coils surrounding the tube. Thus, instead of mechanical scanning, the image dissector utilizes electronic scanning.

4.1.3 Spatial Detection Mode

- a. Multiple Slit - Multiple Detector. This device is most commonly used with a direct reading spectrometer and the selected spectral lines are isolated by exit slits positioned along the focal plane of the spectrometer. An individual photomultiplier detector is placed behind each slit.

- b. Vidicon Tube. The vidicon tube is a television camera type of detector. The dispersed light is incident on the tube. At one end of the tube is an electron gun, which emits a beam of electrons. This beam can be scanned across the tube and can cover the spectral range incident on the tube.
- c. Linear Diode Array. The linear diode array is similar to the vidicon tube except that it does not require an electron beam. Arrays of photodiodes are placed on the focal plane to cover the spectral range of interest. A computer can be coupled with the array to sort out the signal.

4.1.4 Specific Detection Systems

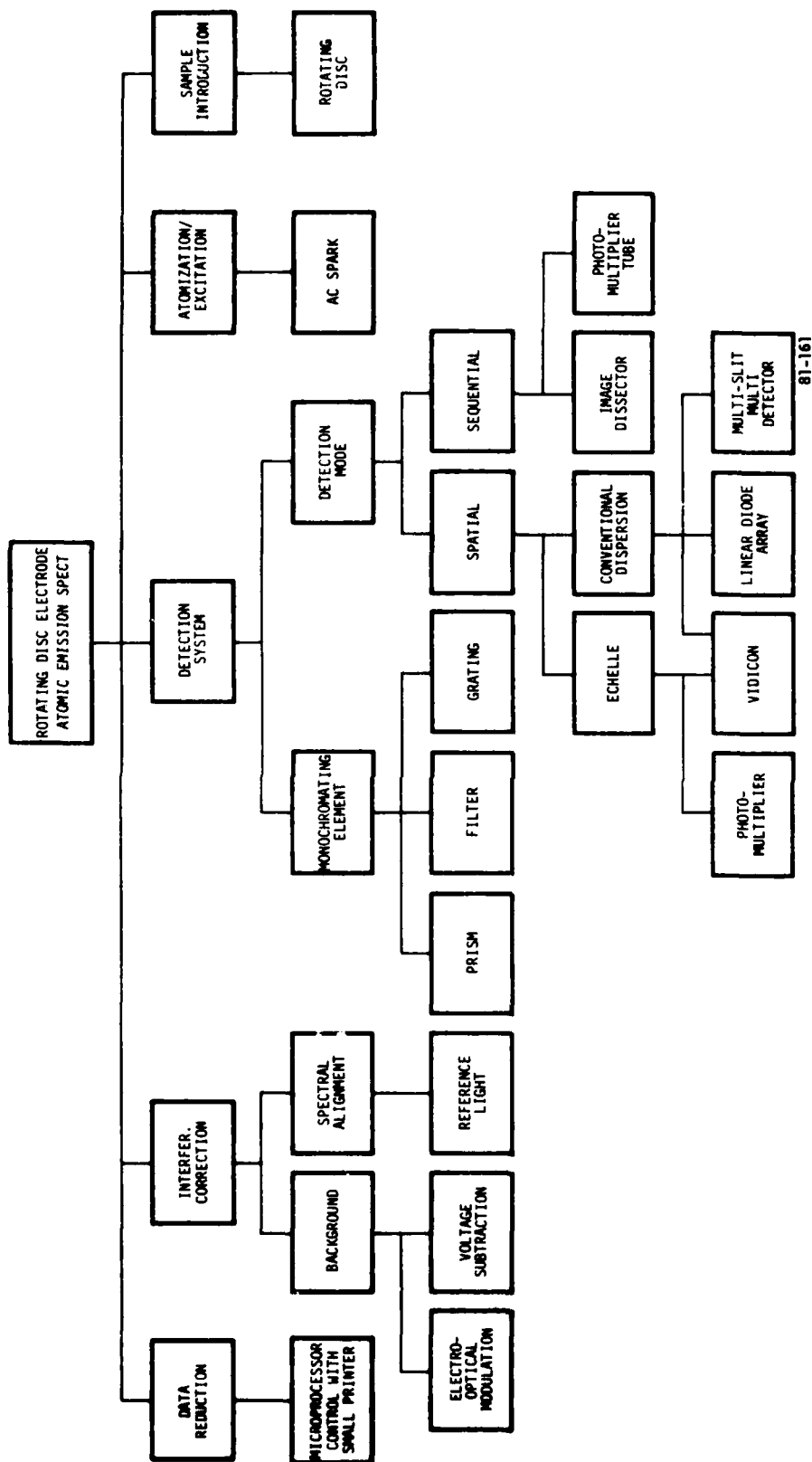
- a. Echelle Spectrometer. By employing a specially designed grating, which has broad, flat grooves ruled for high precision, the Echelle spectrometer differs from the conventional-grating spectrometer. The high orders of the diffraction pattern are used and to avoid the superimposition of orders, a prism is placed so its dispersion is perpendicular to that of the Echelle grating. Thus, a two-dimensional dispersion pattern is produced: a vertical position corresponding to the grating order and a horizontal position corresponding to the wavelength within each order. Photomultipliers, a vidicon tube or an image dissector can be used as detectors. This spectrometer has been employed in the DC plasma AES device.
- b. Resonance Detector. A resonance detector can be used on an AAS instrument. This is a detector consisting of an atomic vapor of the element of interest. The atomic vapor absorbs resonance lines from the light source after it passes through the sample. The absorbed energy is subsequently reemitted, and the signal is detected by viewing at right angles with a photomultiplier.

4.2 DATA REDUCTION SYSTEM. Most of the commercial instruments are equipped with a microprocessor-controlled data reduction system. For the portable wear metal analyzer application, all the controlling functions should be designed with minimum operator interfacing. A printer can be incorporated to record the data.

4.3 ROTATING DISC ELECTRODE ATOMIC EMISSION SPECTROSCOPY. The block diagram shown in Figure 1 along with the explanations illustrate the options available in a rotating disc electrode AES spectrometer.

4.3.1 Sample Introduction System. In the rotating disc electrode AES, the upper electrode is a graphite rod and the lower electrode is a graphite disc, which is approximately 3 to 5 millimeters in thickness and 10 to 15 millimeters in diameter. This disc rotates at 2 to 10 rpm while dipping into a small sample cup filled with the oil. Thus, as the disc rotates, it constantly feeds the sample to the spark, which occurs between the upper electrode and the disc.

4.3.2 Atomization and Excitation Source. The energy of the spark generated between the electrodes serves as an atomization source as well as an excitation source. Modern instruments use a high inductance AC spark because of sensitivity and good signal-to-noise characteristic.



81-161

Figure 1. Instrument Parameters for Rotating Disc Electrode Atomic Emission Spectroscopy

4.3.3 Interference Correction

- a. Spectral Alignment. Usually for the direct reading spectrometer, the multiple exit slits are mounted as a integral assembly. Accurate alignment of this assembly with respect to other optical components is important. A light source, such as a mercury lamp, can be inserted in the optical path to align the instrument.
- b. Background Correction with Voltage Subtraction. The background radiation may come from the light scattering within the optical system. Furthermore, stray light, flame emission and detector dark current may contribute to a background signal. One correction method is to determine the output voltage by averaging several analyses of blank samples. This average voltage can then be subtracted from each signal voltage measured.
- c. Electro-Optical Background Correction. In this correction mode, a deflector is inserted between the entrance slit and the diffraction grating of the spectrometer. The deflector is vibrated in a way that the emission line is alternately on and off the exit slit. The photomultiplier detector positioned behind the slit alternately sees the background signal with and without the emission line, and, therefore, the background can be subtracted out.

4.4 DC PLASMA ATOMIC EMISSION SPECTROSCOPY. The parameters involved in DC plasma are shown in Figure 2. The considerations for the inlet system, source, and background correction are considered here.

4.4.1 Sample Introduction System. In DC plasma AES, the sample is usually diluted with a suitable solvent such as MIBK. The sample is directly aspirated into the plasma flame by means of a peristaltic pump. There is some possibility that other methods of introducing the sample can be used. One such method is by placing the sample into a graphite boat and introducing the boat to the plasma, but the development of this method is unknown.

4.4.2 Atomization and Excitation Source. The plasma jet serves as an atomization and excitation source. The plasma flame is formed by ionized argon (Ar) gas. Historically, two-electrode systems were used to maintain the plasma flame, but the stability was relatively poor. Modern designs have incorporated a three-electrode system to improve the stability. The sample temperature achieved by this three-electrode plasma ranges from 5,000 to 10,000°K.

4.4.3 Background Correction. In principle, background correction techniques used in the rotating disc electrode AES can also be applied to DC plasma AES. Modern DC plasma AES instruments offer features such as software controlled background compensation. A background scan of a blank solution can be stored in the data file and subsequently subtracted from the sample scan.

4.5 FURNACE ATOMIC ABSORPTION SPECTROSCOPY. The parameters involved in furnace AAS are shown in Figure 3.

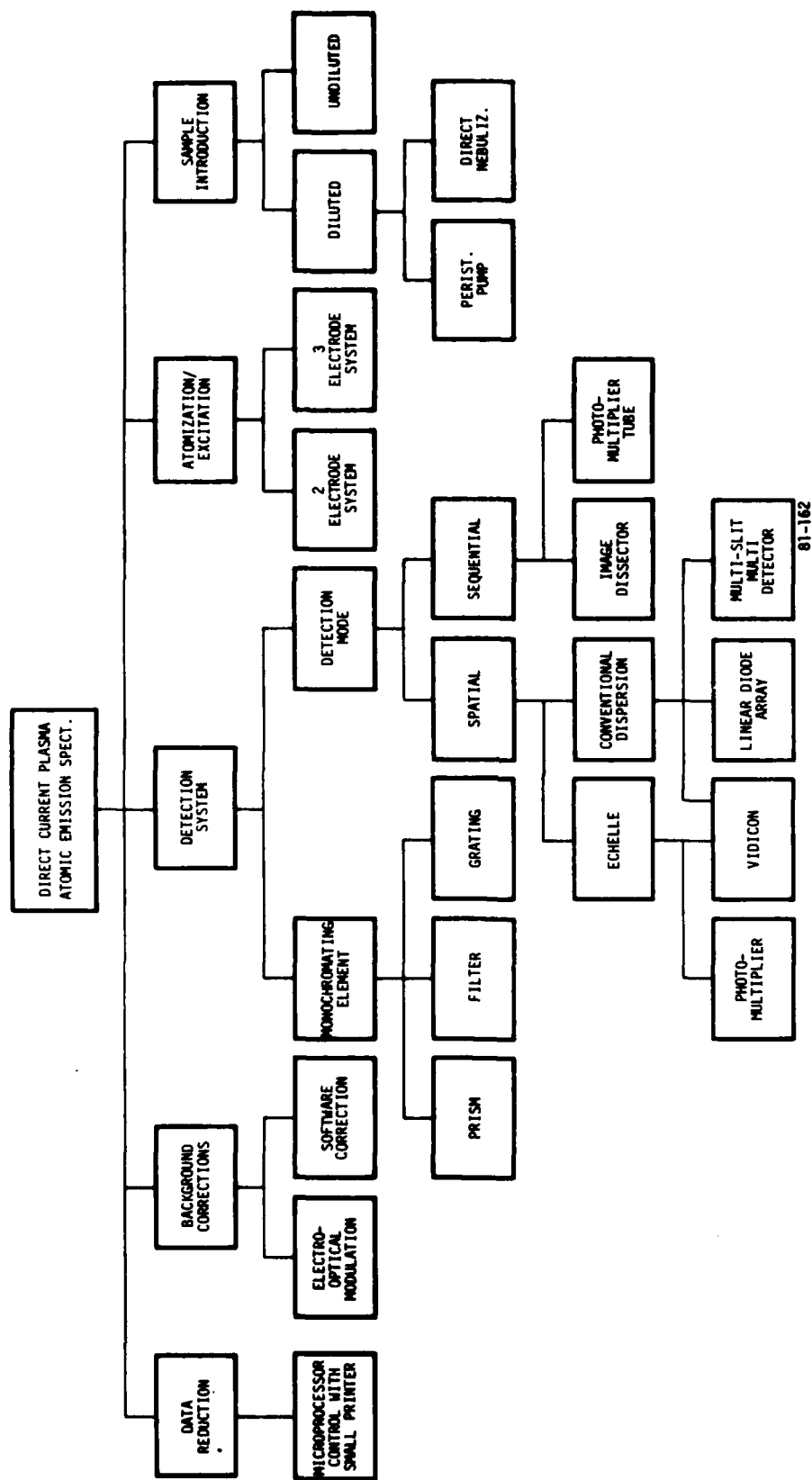
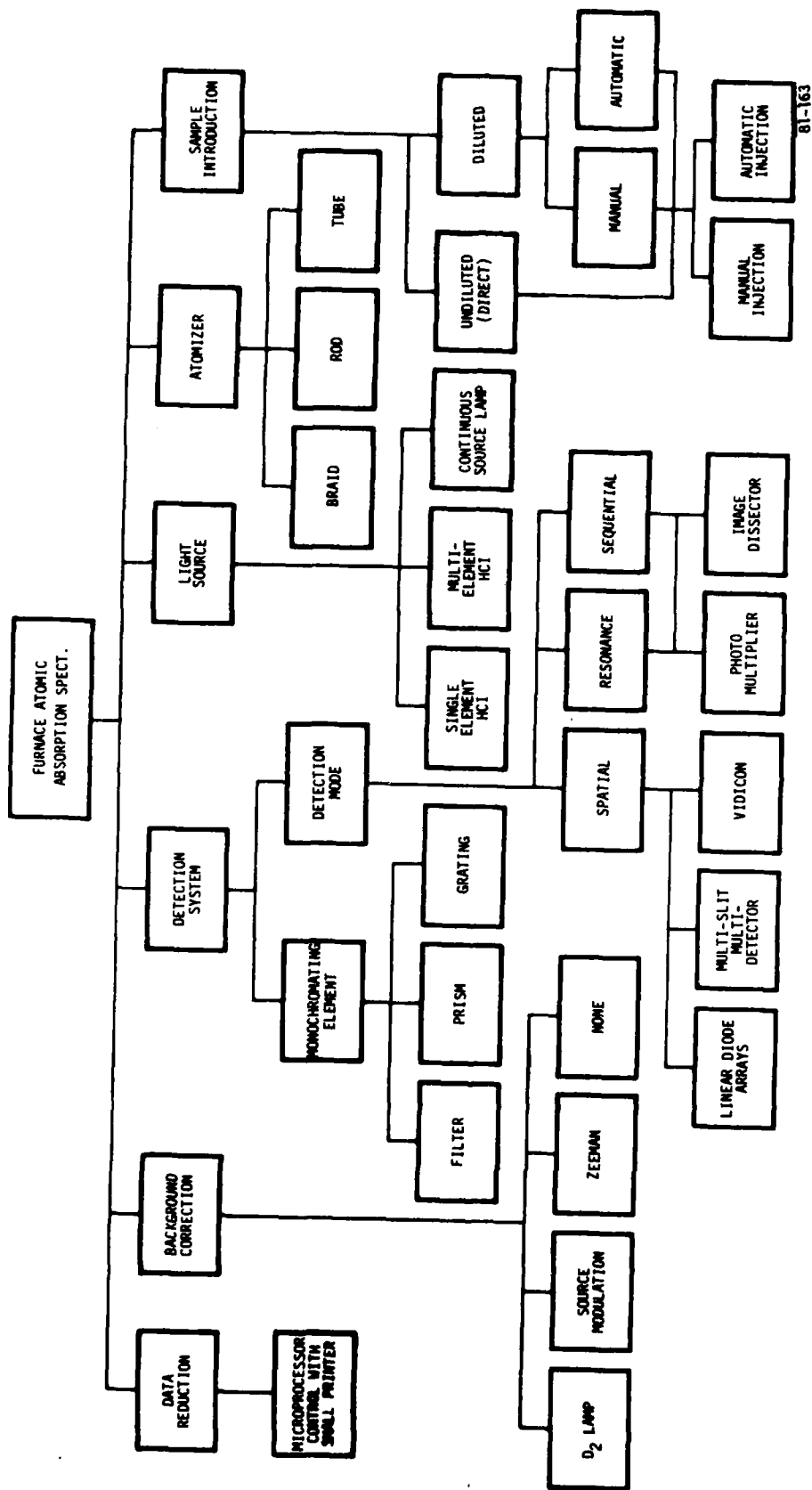


Figure 2. Instrument Parameters for DC Plasma Atomic Emission Spectroscopy



81-163

Figure 3. Instrumental Parameters for Furnace Atomic Absorption Spectroscopy

4.5.1 Sample Introduction. The sample size involved in furnace AAS is on the order of microliters, either diluted or undiluted. Usually the sample is introduced by an autopipette. Modern instruments are equipped with auto-samplers to increase the precision.

4.5.2 Atomization. The atomization of the sample is accomplished by heating the graphite sample holder. This holder can be a tube, rod, or braid, depending on the furnace design.

4.5.3 Light Source. A hollow cathode lamp is usually used as the light source and is a discharge lamp filled with inert gas. The cathode is a hollow cylinder, which is made of the metal corresponding to the spectrum to be produced. The inert gas pressure is a few torr, and the lamp operating temperature is about 500 to 600°K. Single element lamps are most commonly used. However, multielement lamps containing up to six elements are commercially available.

4.5.4 Background Correction

- a. Modulation. The light source in an atomic absorption spectrometer should be modulated in order to differentiate between the emission signal from the elements in the sample and the emission signal from the light source. The modulation can be accomplished by mechanically chopping or by pulsing the lamp itself.
- b. Background Correction With Continuum Source. A sample matrix having a broadband absorption spectra may contribute to the atomic absorption signal, and these additional spectral contributions cannot be removed by source modulation. To cope with these effects, a continuum source (e.g., deuterium lamp) is frequently used as a background corrector where the continuum lamp and the hollow cathode lamp are brought into the light path alternately. The intensity of both light beams is balanced. The matrix molecules absorb light from both sources and the analyte atoms primarily absorb light from the hollow cathode source. Background correction is achieved by subtraction of the absorption signal of the continuum lamp from the absorption signal of the hollow cathode lamp.
- c. Background Correction With Zeeman Effect. In the presence of a magnetic field, the energy levels of an atom split into three or more components. This is called the Zeeman effect. The π component (Δ magnetic quantum number = 0) is polarized parallel to the magnetic field; the σ \pm components (Δ magnetic quantum number ± 1) are polarized perpendicular to the magnetic field. To use the Zeeman effect as a background correction technique, a rotating polarizer is placed in front of the light source to polarize the light, and a magnetic field is used to split the energy levels of the sample atom. The polarized light beams, parallel and perpendicular to the magnetic field, are brought into the atomizer alternately. Only the energy levels polarized parallel to the magnetic field can absorb the light beam polarized parallel to the magnetic field; whereas, the broadband background absorption is not polarized absorbing both polarized light beams equally. Therefore, the background absorption can be subtracted out.

4.6 PORTABLE INSTRUMENT CONFIGURATION. Since no commercial instruments are designed for portable use, redesign and repackaging aimed at reduction of size and weight become necessary. Usually, the details of instrument design are not available in the literature, except for limited information in the manufacturer's brochures. Therefore, only the feasible approaches are discussed below.

4.6.1 Rotating Disc Electrode Atomic Emission Spectroscopy. The best combination of parameters from those shown in Figure 1 would be: the rotating disc for sample introduction; AC spark for the source; diffraction grating, multiple exit slits and photomultipliers for the spectrometer; mercury lamp for spectral alignment; electro-optical correction for background correction; a small printer for data output. The spectrometer may be scaled down or an Echelle spectrometer may be used as an alternative in order to reduce weight.

4.6.2 DC Plasma Atomic Emission Spectroscopy. The best combination of parameters from those shown in Figure 2 would be: a new method for introducing the undiluted sample; a three-electrode system; an Echelle spectrometer; a background compensator; and a small printer for data output. A miniaturized version of the plasma-forming electrodes could possibly be designed to reduce the size of the power supply and the argon consumption.

4.6.3 Furnace Atomic Absorption Spectroscopy. The best combination of parameters from those shown in Figure 3 would be: manual sample introduction with possibly a new design of the pipette for ease of operation; a graphite tube as an atomizer; two multielement hollow cathode lamps to contain all the elements of interest; a grating, multiple slits-photomultipliers for the spectrometer; source modulation and deuterium lamp for background correction; and a small printer for data output.

5. PERFORMANCE PARAMETERS

Parameters related to the practical performance of the three techniques considered in Section 4 are discussed here. Although some of the characteristics are undesirable and could lead to degraded performance, they are not fundamental limitations and can generally be corrected by instrument design.

5.1 MATRIX EFFECTS. Furnace AAS is somewhat subject to matrix effect, commonly seen as physical and chemical interferences.²³ Physical interferences refer to the molecular absorption by the matrix and can usually be compensated for by the background correction techniques discussed in Section 4. A matrix modification technique can also be applied by adding chemicals to increase the volatility of the matrix so that the matrix can be totally removed by charring. Chemical interferences are caused by the elements of interest combining with cations or anions in the sample matrix to form compounds which have different vaporization rates. As a result, the number of ground state atoms of the elements of interest is changed at the temperature at which atomization takes place. The signal can either increase or decrease, depending on the volatility of the compound formed. The use of matrix modification techniques can sometimes alleviate the problem. In general, matching the matrices between the sample and the standard can minimize the matrix effect.

Since the matrix can affect the signal intensities observed, the rotating disc electrode AES also requires closely matched matrices of standard and sample.²⁴ For a given element in different matrices the vaporization rates and the conditions within the source are different during the determination leading to different results.

For DC plasma AES, sample dilution is usually necessary and therefore the technique is less subject to matrix effects than the other techniques.²⁵ The high temperature on the inert atmosphere achieved by the plasma also removes most of the chemical interferences.

5.2 SPECTRAL INTERFERENCE. When spectral lines resulting from the elements in the sample are close together and difficult to resolve, spectral interference occurs. This phenomenon is more severe in AES than in AAS. In AE spectroscopy, every element in the sample contributes to the emission signal and therefore interference is more likely to occur. This leads to the requirement for a high resolution spectrometer, which, practically, is difficult to make portable. Commercial instruments usually employ spectrometers with a spectral bandpass of 0.1 Å to 0.3 Å. For the portable wear metal analyzer application, the elements in the oil sample are limited to wear metals and the twenty elements in the Conostan D-20 standard were therefore used to study the spectrometer requirement. As a result, a maximum spectral bandpass of 0.5 Å was estimated. An evaluation of the parameters involved in spectrometers is discussed in Appendix E.

23. Matousek, J.P., "A Carbon Rod Atomizer for Atomic Absorption Spectroscopy", American Laboratory, June 1971

24. Winefordner, J.D., ed., "Trace Analysis and Spectroscopic Methods for Elements", Wiley-Interscience, New York, (1976)

25. Ibid.

In atomic absorption, only the elements in the sample having spectral lines matching the emission lines from the light source contribute to the absorption signal. The light source is usually modulated in order to differentiate the emission signals from other elements in the sample. A spectral bandpass between 2 Å to 10 Å is commonly used in commercial instruments. When using multielement lamps, the spectral complexity increases and a smaller bandpass should be used.

For DC plasma AES, the background emission from the plasma source imposes another limitation on the spectral selection.

5.3 PARTICLE SETTLING RATES. Suspended metal particles in the oil sample have a tendency to settle to the bottom of the sample container. The settling rate is a function of the viscosity of the sample solution, the particle size and the density of the metal. Presently, standards prepared by the Tri-Services use grade 1100 oil as a base, which has a viscosity of approximately 230 centistokes at 100°F. Two other commonly used oils, MIL-L-7808 and MIL-L-23699, have viscosities of 13.8 and 25 centistokes at 100°F, respectively.

A calculation of settling rates for different particle sizes is shown in Appendix F. As an example, for a 5 micrometer iron particle in MIL-L-7808 oil, the settling rate is approximately 0.5 millimeter/minute. When the sample is diluted with a solvent, the settling rate increases, since the rate is inversely proportional to the viscosity.

5.4 PARTICLE SIZE AND ATOMIZATION. In both the AAS and AES process, the metal particles (solute) in the sample are atomized before absorption or emission can occur. The final step of atomization is the vaporization which converts the solute into atomic vapor. The vaporization of solute particles has been studied in flame spectrometry and the mechanisms are summarized below.²⁶

- a. Heat-Transfer Controlled Vaporization. Relatively volatile solutes are heated to their boiling points and vaporized. The vaporization rate is a function of the flame temperature and the thermal conductivities of the flame gases and solute vapor.
- b. Mass-Transfer Controlled Vaporization. The vaporization rate is limited by the diffusion of the gaseous solute away from the particle and the rate is a function of the diffusion coefficient of the solute vapor, the solute volatility and the flame temperature.
- c. Refractory Solutes. The salts or oxides of some elements (e.g., tungsten, zirconium) have melting points higher than the flame temperature. The atom production is then probably due to sublimation of the heated solute and the surface reactions on the dried particle.

26. Bastraans, G.J., G.M. Hieftje, "Investigation Into the Vaporization of Individual Solute Particles in Flame Spectrometry", Analytical Chemistry 46:7, (1974), p. 901

- d. Non-Volatile Solutes. For solutes having boiling points higher than the flame temperature, boiling of the molten solute will not occur. The vaporization rate will then depend on the vapor pressure of the solute at the flame temperature.

It is uncertain whether the above mechanisms can be directly applied to other atomization devices. Generally, the efficiency of the vaporization of the solute is a function of the residence time and the temperature of the atomization device, thus explaining why the short residence time (a few milliseconds) and the relatively low temperature (3000°C) of the flame AAS technique results in an incomplete burn of large particles. The ICP AES technique has a much better vaporization efficiency because of the higher temperature and slightly longer residence time. For the furnace AAS technique the sample is in direct contact with the furnace tube and because the sample can stay in the high temperature region for as long as a few seconds, the furnace AAS is essentially particle-size independent.

When sample introduction involves aspiration, as in flame AAS or plasma AES, the aspiration of particles also affects the total atomization. The atomization efficiency is the product of the efficiency of aspiration and of vaporization. Taylor reported that in a case study using the flame AAS technique, the aspiration efficiency for a 3 μm particle was only 25 percent.²⁷

27. Taylor, J.H., T. T. Bartels, N.L. Crump, "Behavior of Metal Particles Compared to Organometallic Compounds Measured by Flame Atomic Absorption Spectrophotometry", Analytical Chemistry, 43:13, (1971), p. 1780

6. RATING OF TECHNIQUES

6.1 RATING CRITERIA. The evaluation of the top three methods is according to the prioritized criteria in the Statement of Work: 1) portability, 2) cost, 3) multi-element capability, 4) particle-size dependency, and 5) power consumption. Most of these criteria are discussed in previous sections, and they are summarized below:

6.1.1 Portability

- a. Furnace AAS. The atomic absorption spectrometer can be made portable. The lightest commercial flame AAS instrument weighs only 30 pounds excluding gas supplies for the burner.²⁸ The power supply for the furnace would add weight to the instrument and the need for argon gas also imposes weight limitations on portability. However, the gas consumption is relatively low, and a light weight gas cylinder could be incorporated as a part of the instrument.
- b. Rotating Disc Electrode AES. The main limitation of this technique is the high resolution requirement of the spectrometer. To maintain the alignment of a high-resolution instrument in a field-use environment is very difficult, and the requirement would demand a strong, heavy support for the optics.²⁹ The current JOAP base unit weighs approximately 500 pounds.
- c. DC Plasma AES. The high argon gas consumption becomes a serious limitation for this technique. The argon usage for commercial instruments is approximately 7 liters/minute continuously.³⁰ This rate of consumption makes the mounting of a small cylinder on the instrument impractical. Commercially available DC plasma units weigh approximately 250 pounds.

6.1.2 Cost. It is difficult to make a cost estimate for a ruggedized, portable version of all three instruments. Therefore, the prices for commercial instruments are listed for comparison.

- a. Furnace AAS. A microprocessor-controlled, fully automated furnace costs approximately \$25,000 to \$30,000.
- b. DC Plasma AES. Approximately \$40,000 to \$50,000.
- c. Rotating Disc AES. (Ruggedized version) approximately \$75,000.

28. Carben Mfg., Inc., 10616 Sentinel, San Antonio, Texas 78217

29. Baird-Atomic, Ltd., Warner Dr., Ind. Estate Rayne Rd., Baintree, Essex, England

30. Spectrametrics, Inc., 204 Andover Street, Andover, MA 01810

6.1.3 Multielement Capability

- a. DC Plasma AES With Echelle Spectrometer. This technique is versatile for multielement analysis. Up to twenty wavelengths can be selected at one time and the change of wavelength selection is accomplished by changing a cassette positioned at the focal plane of the spectrometer. The cassette acts as a masking device that allows only the wavelengths of interest to pass.
- b. Rotating Disc AES With Direct-Reading Spectrometer. This technique can analyze up to twenty elements at one time, but making a change of wavelength selection on the direct-reading spectrometer is difficult.
- c. Furnace AAS. The elements to be analyzed must be included in the light source. For the portable wear metal analyzer, nine elements of interest can be housed in two multielement lamps. However, if analysis of any additional element is desired, the lamps must be changed.

6.1.4 Particle-Size Dependency

- a. Furnace AAS. The furnace AAS technique is essentially a particle-size independent technique because large metal particles can stay in the atomization environment for a relatively long time. A practical limitation is the statistics of the large particles contained in the sample as described in Appendix G.
- b. Rotating Disc AES. The rotating disc AES technique exhibits some particle-size dependency, which is probably due to the short residence time of the sample in the AC spark. The settling rate for large particles in the oil sample might also contribute to this particle-size dependency.
- c. DC Plasma AES. The nebulization efficiency of the sample introduction system and the different viewing heights required for different sizes of particles makes DC plasma AES particle-size dependent.

6.1.5 Power Consumption. All the instruments consume reasonable power and can be used on either 110 or 220 V power lines. Furnace AAS consumes relatively high peak power, but the average power is reduced because of the short duty cycle.

6.2 RATING. The three techniques are ranked according to their suitability for development of a portable wear metal analyzer:

- a. Graphite Furnace Atomic Absorption Spectroscopy.
- b. Rotating Disc Electrode Atomic Emission Spectroscopy.
- c. DC Plasma Atomic Emission Spectroscopy.

These methods are further compared in Table 3 which also shows the reasons for our ranking.

TABLE 3. Comparison Table of Top Three Methods

Criteria in The Statement of Work	Graphite Furnace AAS	RDE/AES	DC Plasma/AES
Measure all 9 Elements	Yes	Yes	Yes
Adequate Sensitivity	Yes	Yes	Yes
Fast Analysis (< 5 min)	Yes	Yes	Yes
Independent of Particle Size	Yes	No	No*
Good Repeatability	Yes	Yes	Yes
Use Conostan Standards	Yes	Yes	Yes
Independent of Viscosity	Yes	No	Yes
Suitable for 110 or 220 V	Yes	Yes	Yes
Gas Flow Required**	1 liter/minute argon (during analysis)	None	7 liters/min argon (continuously)
Cost**	Medium	High	High
Sampling	Discrete	Continuous	Continuous
Power Required	Medium	Medium	Medium
Maintain Spectral Alignment Under Field Use Environment (Potential for Ruggedness)	Yes	Difficult	Difficult

*May be alleviated by using a different sampling method

**Based on commercial instrument

7. CONCLUSION

An ideal technique for the development of a portable wear metal analyzer should meet all the "musts" and "goals" criteria outlined in Section 3. Unfortunately, no instrumental technique exists that meets all of these criteria so design trade-offs must be made in the development of such an instrument. In the first part of this study, the effort was focused on eliminating the techniques which failed to meet the basic requirements. Seven of the ten techniques were rejected because of fundamental limitations within the methodology. In the second part of the study, the practical aspects and limitations of each of the three remaining techniques were then considered, relevant to their effect on the feasibility of developing a portable instrument. The three techniques were then ranked according to their suitability for further development. The conclusions of this feasibility study are based on our best judgment, using the technical information available to date, and could be subject to change as new knowledge or breakthroughs become available.

The graphite furnace atomic absorption spectroscopic technique was selected as the best candidate for the development of a portable instrument. Due to the need for a portable instrument for field use, the atomic absorption spectroscopic technique is preferable to the atomic emission spectroscopic technique because the minimum spectral bandpass requirement for the spectrometer is increased by a factor of ten. Maintenance of optical alignment under environmental conditions of shock, vibration and temperature can therefore be achieved with a smaller and lighter optical system. The graphite furnace technique, utilized to atomize and excite the metal components of the oil sample, has more than adequate sensitivity for this application and is also particle-size independent over the particle-size range encountered in engine oils. Time-averaged power requirements are low, even though high power is required briefly for furnace heating. The main consumables' requirement is inert gas (usually argon) for the removal of air, combustion products and sample atoms from the furnace during heating. Total inert gas consumption is very low compared to plasma atomic emission spectroscopic techniques.

Portable multielement atomic absorption instruments are not available commercially and, therefore, some key issues should be experimentally evaluated before acceptable design trade-offs can be realized. These key issues are: sample introduction with a minimum of pretreatment; establishment of an optimum furnace temperature cycle, which will atomize all required elements yet avoid the saturation of some signals; and avoidance of interferences from metals that are present in the oil sample, but are not being analyzed.

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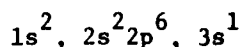
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APPENDIX A

FUNDAMENTAL PRINCIPLES OF INSTRUMENTAL TECHNIQUES

Basic theories of the instrumental techniques involved in this study are described in this section. Some fundamental properties and limitations for each of them are also discussed. Four of the techniques studied, namely, atomic absorption, atomic emission, X-ray fluorescence, and radioisotope technique, are atomic spectroscopic methods. Colorimetry is a molecular spectroscopic method in which the elements form complex ions with organic reagents and then absorb light. Since more chemistry is involved, the technique of colorimetry will be treated separately.

1. ATOMIC MODEL. Electrons in an atom occupy various discrete energy levels. The quantum number n (where $n = 1, 2, 3, \dots$) defines the energy levels. These levels are further divided into sub levels defined by the quantum number l . To avoid confusion, a letter code has been adopted. Thus, the letters s, p, d, f are used instead of $l = 0, 1, 2, 3$. For example, the sodium (Na) atom has 11 electrons and the lowest level (ground state) atom can be written as:



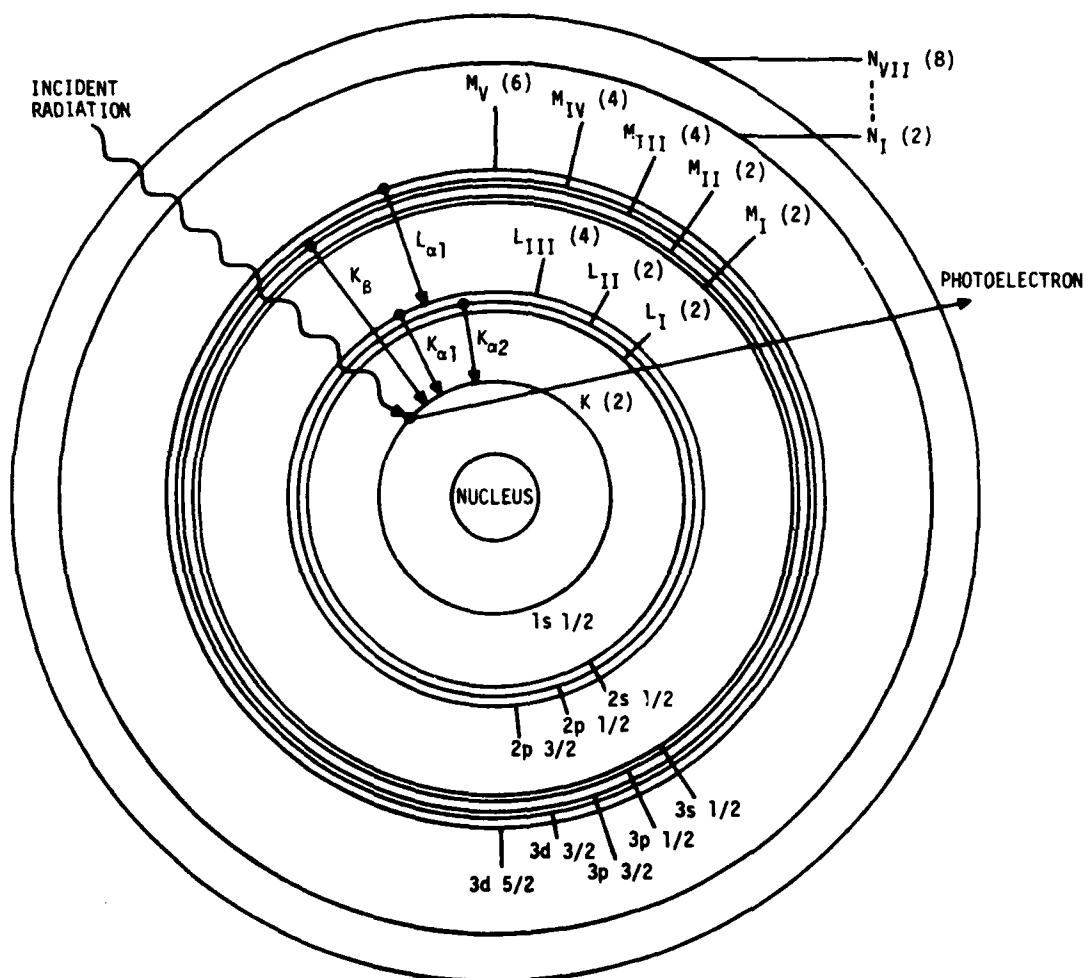
The superscript represents the number of electrons in the corresponding level.

The structure of an atom can also be visualized as shown in Figure A-1. The electrons occupy the shells designated K, L, M, N which correspond to $n = 1, 2, 3, 4$. These shells are divided into subshells, the l numbers of which are shown in the lower portion of the figure. The energy levels are discrete in nature and the transition of electrons between these energy levels results from absorption or emission of electromagnetic radiation. The detection of the radiation signal thus forms the basis of spectroscopic methods.

1.1 OPTICAL SPECTROSCOPY. In optical spectroscopy, the transition of electrons occurs in the outer shells; the energy involved is of the order of several electron volts (eV). In the case of the sodium atom in its ground state, the outer electron is in the $3s$ level. Transition lines terminating in the ground state are called resonance lines. The electron transition between $3s$ and two $3p$ levels results in a doublet at a wavelength of 589.6 nm and 589.0 nm, the well-known sodium D lines.

1.2 X-RAY SPECTROSCOPY. The energy involved in X-ray spectroscopy ranges from a few kiloelectron volts (keV) to tens of keV. This energy is due to transitions between inner shell electrons. Transitions between the L - and K -shells, and the M - and K -shells are designated as $K\alpha$ and $K\beta$ respectively. Usually, the $K\alpha$ line is the most intense. Details of the X-ray method are discussed in later sections.

1.3 NUCLEAR SPECTROSCOPY. A nuclear reaction can be initiated by bombarding a target nucleus with nuclear particles or gamma rays. The excited nucleus is said to be radioactive due to radiation emitted as it undergoes radioactive decay. Radiation is emitted either from the nucleus itself or



UPPER PART SHOWS THE NOTATION IN X-RAY SPECTROMETRY, THE NUMERAL IS THE NUMBER OF ELECTRONS IN THAT ORBITAL WHEN FULL.

LOWER PART SHOWS THE NOTATION IN OPTICAL SPECTROSCOPY. THE HALF INTEGER GIVES THE VALUE OF THE QUANTUM NUMBER OF THE TOTAL ANGULAR MOMENTUM.

81-155

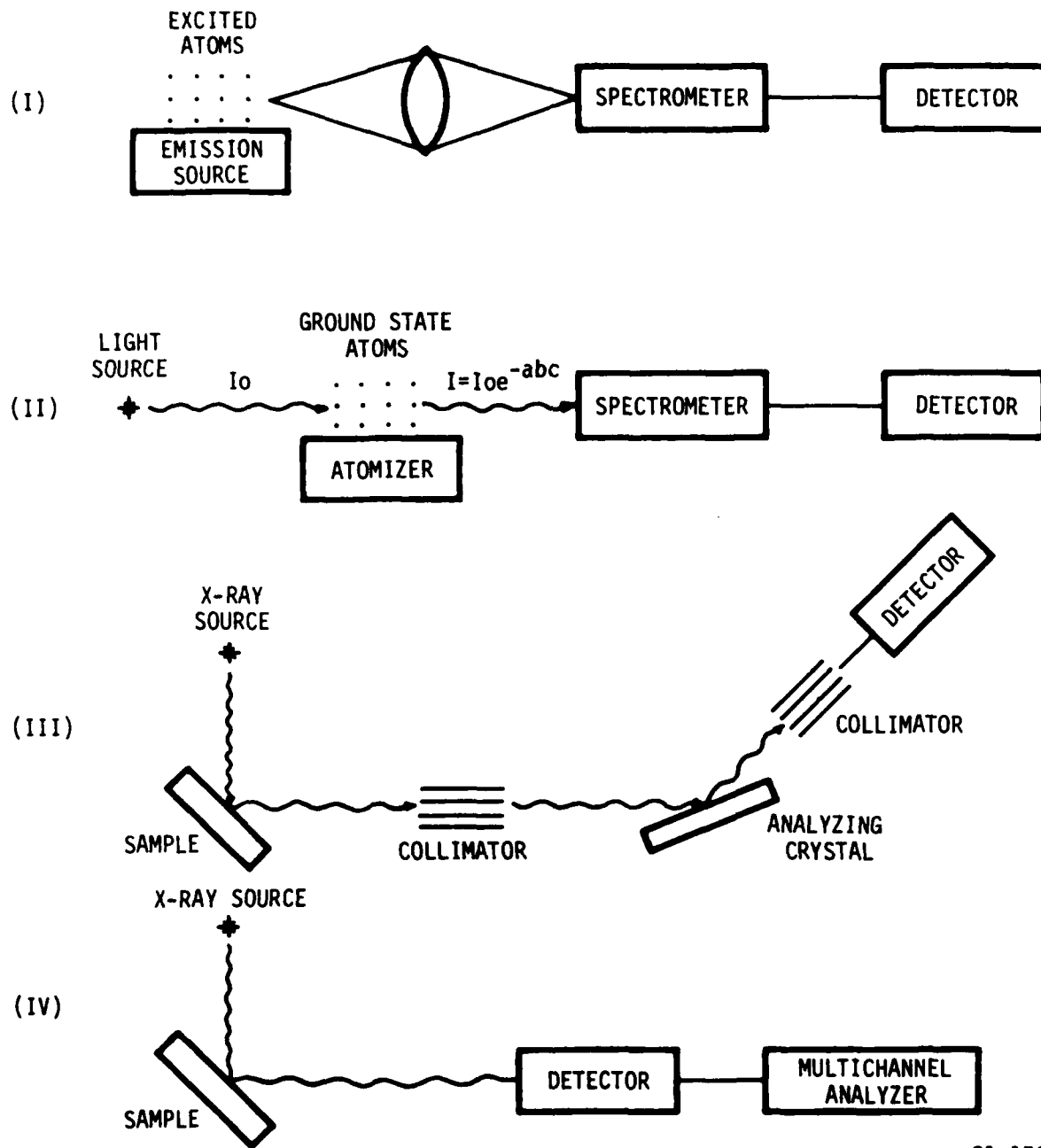
Figure A-1. Atomic Model

as a result of changing the orbital electron. Types of radiation include alpha particles, beta particles and gamma radiations. The energy involved is generally in the keV and Mega electron volts (MeV) region.

2. TECHNIQUE DESCRIPTIONS. Ten techniques, as required by the Statement of Work, were studied and their basic principles are briefly described. Other potential methods, such as atomic fluorescence spectroscopy (AFS), were also explored. Due to the lack of commercial AFS instruments, development in this area is relatively limited; however, several references are listed under MISCELLANEOUS in the Bibliography.

2.1 ATOMIC EMISSION SPECTROSCOPY. An atom in its ground electronic condition can absorb energy and be transferred to an excited state. The excited atom can then return to the lower energy state by emitting a photon. As an example, in a sodium atom a 3s electron can be promoted to one of the 3p levels by an excitation source, such as a spark, plasma flame, or graphite furnace. A photon with a wavelength of 589 nm is then emitted by a 3p electron when returning to the 3s level. Transitions among other energy levels can also occur, resulting in different emission lines with different intensities. Block diagrams showing the atomic emission, atomic absorption, and X-ray fluorescence methods are shown in Figure A-2.

- a. AES With a Rotating Disc Electrode. Excitation of the atoms is achieved by an AC spark source that employs a high voltage discharge of short duration. The lower electrode is a graphite disc, which rotates in a vertical plane and dips into a cup containing the sample solution. The counter electrode is a graphite rod placed vertically a few millimeters above the rotating electrode. As it rotates, the disc picks up fresh solution and presents it to the spark source, and the emission lines from the sample are detected by a spectrometer. In order to quantitatively determine the concentration of the unknown sample, the emission signal must be compared to a calibration curve established by measuring a set of standards with known concentrations. Daily calibrations are needed to insure the proper setting of the instruments. Calibration methods apply to all the techniques described in this report.
- b. AES With a Graphite Furnace. Basically the excitation of the atoms is accomplished by passing a high electrical current through a graphite tube into which the sample has been placed. The open end of the tube is aligned with a spectrometer which detects the emission lines.
- c. AES With Plasma Flame. The two most popular types of plasma are considered here, namely, inductively coupled plasma and DC plasma.
 1. Inductively Coupled Plasma. An induction coil connected to a RF power supply is placed outside a quartz tube through which argon gas is passing. High frequency currents flow in the induction coil and generate an oscillating magnetic field. The magnetic field, in turn, induces the ions and electrons (initially produced by a Tesla coil) to flow in annular paths inside the quartz tube. Since the magnetic field varies with time, the electrons and ions are accelerated in each half cycle.



81-156

Figure A-2. Schematic Diagrams for (I) Atomic Emission
 (II) Atomic Absorption (III) Wavelength-Dispersive
 X-Ray Fluorescence (IV) Energy-Dispersive X-Ray Fluorescence

The ions and electrons meet resistance to their flow and resistive heating occurs. The temperature of ICP can reach 10,000°K. This high temperature and the doughnut shape of the flame produces good excitation efficiency for most elements, including refractory metals.

2. DC Plasma. Conventionally, a DC plasma is formed by two electrodes. The cathode is a water-cooled, thoriated, tungsten rod and the anode is a graphite plate. Using argon gas as the medium for the plasma, the sample is sprayed between the rod and the plate. An insulated graphite ring is mounted in the gap between the electrodes to confine the plasma. Unlike the ICP, only a small fraction of the sample aerosol particles actually enters the plasma. A new design of DC plasma employs three electrodes with the plasma being formed between two carbon anodes and a tungsten cathode in an inverted-Y configuration. In this design the stability is better than that of the two-electrode design.

2.2 ATOMIC ABSORPTION SPECTROSCOPY. In the atomic absorption process, a light source emits photons, which pass through the sample vapor produced by an atomization device. The decrease in intensity of certain emission lines - due to the absorption by appropriate atoms in the sample - can be measured. In the example of the sodium atom, a sodium hollow cathode lamp emits the characteristic lines of sodium which are, in turn, directed toward the spectrometer. One of the lines is selected as the detection line, as for example, 589 nm. The 3s electrons of the sodium atom in the sample absorb this line and are transferred to the 3p level. The reduction in intensity of this emission line at the spectrometer is proportional to the concentration of the sodium atom in the sample.

In order for absorption to occur, the sample must be in the atomic form. The three types of atomization devices discussed here are flame, graphite furnace and plasma.

- a. AAS with Chemical Flame. A mixture of air and acetylene or acetylene and nitrous oxide is normally used as the fuel for the flame. The sample solution is aspirated through a nebulizer and sprayed as a fine aerosol into a mixing chamber. The sample aerosol then mixes with the fuel and is carried to the burner head where the atomization occurs. The light emitted from the source is aligned along the flame path and the spectrometer. The flame is the most popular atomizing device and gives a simple, accurate and fast analysis.
- b. AAS with Graphite Furnace. A graphite furnace is a flameless atomizing device. As discussed in Graphite Furnace AES (Appendix A, Paragraph 2.1b), a large electric current is passed through a graphite tube in which the sample is placed. The heating of the tube provides the energy to atomize the sample. With this device, most of the elements can be measured at concentrations two to three orders of magnitude lower than that of the flame AA.

- c. AAS with Plasma Flame. The plasma sources employed in the AE process can be coupled to the AA system and used as an atomization device. Theoretically, the high temperature plasma source should give better atomization efficiency. However, little published work has been done in this area.

2.3 X-RAY FLUORESCENCE. When an atom is bombarded by an energetic electron or photon, it can be ionized by losing one of its inner electrons. The atom then rearranges itself by shifting an electron from an outer shell into the vacancy left by the departed electron. The resultant surplus energy is emitted as an X-ray. This radiation, called the characteristic radiation, is representative of the atomic structure of each element. As shown in Figure A-1, the electron on the K-shell is expelled by the incident radiation. The atom becomes unstable because a vacancy is created in the K-shell. The stability can, however, be regained by shifting an electron from the L-shell. The difference in energy between the two shells is emitted as an X-ray photon, and the wavelength is characteristic of the atom. The transition from the L-shell and the M-shell to the K-shell is called $K\alpha$ and $K\beta$ radiation respectively. A numerical subscript is generally used to denote a particular subshell. Some of these notations are shown in Figure A-1.

In X-ray fluorescence spectroscopy, the incident radiation is generated by an X-ray tube or a radioisotope source. The characteristic X-ray emitted by the sample can be measured by two modes of detection: either wavelength-dispersive or energy-dispersive. These two modes are described below.

- a. Wavelength-Dispersive XRFS. Dispersion is achieved by using the specific diffracting property of a single crystal. The fluorescent radiation is collimated and diffracted by the crystal located in the center of a goniometer and then measured by a detector. Commonly used detectors are semiconductor detectors or proportional counters.
- b. Energy-Dispersive XRFS. In the energy-dispersive mode, all the X-ray radiations are directed toward the detector. Since different characteristic lines carry various energies, they produce different pulse heights (number of electrons) in the detector. A multichannel analyzer is employed to sort out the pulses according to their amplitude.

2.4 RADIOACTIVE TAGGING. The radioactive tagging (tracer) method involves creating radioactive nuclei by irradiation and measuring the subsequent radioactivity. This technique was at one time popular in some medical applications. To apply the tagging technique to wear metal analysis, the engine parts such as bearings and piston rings, could be made radioactive and the radioactivity in the oil would then reflect the wear information.

Generally, the radioactive nucleus of an element can be created by bombarding it with neutrons. The type of subsequent radiation produced by the element depends on the decay scheme of that radioactive nucleus and can be an alpha particle, a beta particle, or gamma radiation. For a nucleus to be capable of releasing alpha particles, two protons and two neutrons, it must be relatively large itself. Beta and gamma radiations are more commonly encountered and they can be detected by a sodium iodine (NaI) crystal or proportional counter.

3. INHERENT CHARACTERISTICS OF THE TECHNIQUES. The inherent advantages and limitations for the suitability of a portable wear metal analyzer are discussed in this section. That is, unless some major breakthrough in technology occurs, the properties cannot be changed easily. Emphasis is given to the key parameters of this application, and these considerations will form the basis for the selection and elimination of techniques.

3.1 MULTIELEMENT CAPABILITY

- a. Atomic Emission Spectroscopy. AES is the most versatile multielement technique. Commercially available multielement AE units can detect from 20 to 60 elements simultaneously, depending on the type of instrument.
- b. Atomic Absorption Spectroscopy. AAS was not considered a multielement technique in general because of the need for individual light sources for each element. Although a continuum source has been proposed, the overall results were not satisfactory. For analyzing a limited number of elements, one or more multielement hollow cathode lamps can be used, and elements can be measured simultaneously. However, it is less versatile than AES.
- c. X-ray Fluorescence Spectroscopy. XRFS is a versatile multielement technique and can detect most of the elements in the periodic table. However, XRFS generally needs different X-ray tubes for different groups of elements to attain optimum sensitivity.
- d. Radioactive Method. Almost every element in the periodic table can be made radioactive. The main consideration for wear metal analysis is to find an adequate half-life for the element of interest. The half-life should be greater than one year but less than 50 years, in order to insure that adequate activity persists over the life of engine components and that disposal of used parts creates no other problems.

3.2 DETECTION LIMIT

- a. Atomic Emission Spectroscopy. The detection limit for most elements is in the sub-ppm region which is adequate for wear metal analysis.
- b. Atomic Absorption Spectroscopy. The detection limit is in the sub-ppm region for flame AAS and ppb region for furnace AAS.

- c. X-ray Fluorescence Spectroscopy. The detection limit is in the ppm region for atomic numbers larger than 20. The major limitation for X-ray detection is the scattered background radiation resulting from the continuum produced by the X-ray tube.
- d. Radioactive Technique. It is difficult to define the detection limit for radioactive techniques in general. In the case of gamma ray spectra, the detection limit is in the ppb region.

3.3 PORTABILITY

- a. Atomic Emission Spectroscopy. AES instruments are relatively difficult to make portable. The major hurdle is the need for a large spectrometer to maintain the high resolution requirement. For inductively coupled plasma AES, the requirement for a large RF power supply adds to the system weight and size.
- b. Atomic Absorption Spectroscopy. AAS instruments can be made portable, and light weight commercial instruments do exist. However, the need for gases is a drawback.
- c. X-ray Fluorescence Spectroscopy. Portable wavelength-dispersive and energy-dispersive spectrometers are commercially available. However, the detection limits of the portable instruments are poorer than the laboratory instruments.
- d. Radioactive Technique. Although proportional counters are relatively small in size, this detector can even be on line which is the major advantage of using the radioactive technique.

3.4 PARTICLE SIZE

- a. Atomic Emission Spectroscopy. The AES process is somewhat particle-size dependent. It was reported in several JOAP reports that the AES method failed to detect particles larger than 8 μm in diameter. The mechanism for this limitation was, however, not clear. For DC plasma AES, the sample is conventionally introduced into the plasma flame by the aspiration method and the aspiration efficiency is particle-size dependent. Furthermore, the viewing height for the detector is normally optimized for small particles and therefore large particles are usually not detected.
- b. Atomic Absorption Spectroscopy. Flame AAS is particle-size dependent for particles above a few μm in diameter. Because the sample is continuously aspirated into the flame, the residence time for the sample in the optical path is only a few milliseconds, and this short residence time results in an incomplete burn of the sample. For furnace AAS, large particles can reside in the furnace tube as long as several hundred milliseconds for complete atomization, thus making furnace AAS essentially particle-size independent.

- c. X-ray Fluorescence Spectroscopy. The particle-size effect for XRFS is mainly related to the depth of the penetration of the incident radiation. Since the absorption of x-rays by the sample follows Beer's law, the particle-size effect for different elements can be calculated by their mass absorption coefficients. In general, for 5 μm particles the intensity of the signal would be reduced from 60 to 80 percent of its value compared with the same mass concentration of smaller particles.
- d. Radioactive Technique. The particle-size effect is also related to the depth of penetration. However, due to the large radiation energy involved, this effect is considered insignificant.

3.5 RESOLUTION AND SPECTRAL INTERFERENCE

- a. Atomic Emission Spectroscopy. A high resolution spectrometer is needed for the AE instrument. In the AES process every element in the sample contributes an emission signal and the spectral interference is severe. Generally a spectral bandpass of 0.1 \AA to 0.3 \AA is required.
- b. Atomic Absorption Spectroscopy. In the AAS process the detector measures the reduction in signal emitted from the light source. Therefore, one deals with known spectral lines emitted by the hollow cathode lamps. For single element AAS, a spectral bandpass of 2 \AA to 10 \AA is sufficient.
- c. X-Ray Fluorescence Spectroscopy. X-ray spectra are simpler than optical spectra. However, the resolution for energy-dispersive XRFS is relatively low (150 eV). The $K\alpha$ line of element with atomic number Z is therefore still unresolved from the $K\beta$ line of element $Z-1$ throughout the important region from $Z = 19$ to $Z = 28$.
- d. Radioactive Technique. Gamma rays are monoenergetic so that detectors can resolve two gamma rays of nearly similar energy. Beta particles are emitted with a range of energies lying between zero and the maximum energy so that available detectors cannot resolve two beta particles of nearly similar energy.

3.6 ANALYSIS TIME

- a. Atomic Emission Spectroscopy. The AES process allows fast analysis and one to two minutes per sample is sufficient.
- b. Atomic Absorption Spectroscopy. Analysis time for flame AAS requires less than one minute per sample. For furnace AAS, two to three minutes is needed because the sample must be charred before the analysis.
- c. X-Ray Fluorescence Spectroscopy. Normally the counting time for XRFS is 100 seconds. However, the signal-to-noise ratio is proportional to the square root of the counting time. Therefore for a low concentration measurement, a longer counting time would improve the detection limit.

- d. Radioactive Technique. The signal-to-noise ratio also improves as a longer counting time is used. Due to the good sensitivity of the technique, a long counting time is generally not necessary.

3.7 MATRIX EFFECT

- a. Atomic Emission Spectroscopy. In the rotating disc electrode AES method, the different viscosities of the oil samples will affect the sample pickup. For plasma AES, the sample uptake rate or nebulization efficiency may also be affected by viscosity but sample dilution can generally alleviate the problem.
- b. Atomic Absorption Spectroscopy. For flame AAS the matrix effect is mainly due to the viscosity and the surface tension of the oil. In furnace AAS the matrix effect is due to the incomplete burn of the sample resulting in broadband background absorption.
- c. X-Ray Fluorescence Spectroscopy. The matrix effect in XRFS is mainly absorption and enhancement. When the excited atoms of the element are deep within the sample matrix, the characteristic radiation which is produced has to travel through the volume of the matrix in order to leave the sample. The measured photons actually leaving the sample will be less than the number initially produced due to absorption. The enhancement effect is the counterpart of the absorption effect. When a characteristic line of element A lies just to the high energy side of element B, A is said to be absorbed by B; B is, in turn, enhanced by A. For analysis of metals in an oil matrix, the effective volume of the sample is, therefore, only a thin layer.
- d. Radioactive Technique. Gamma ray detection is less affected by the oil matrix, but the absorption effect makes the detection of low energy beta particles in an oil matrix very difficult.

4. COLORIMETRY. Colorimetry is a technique which involves measuring the absorbance of light passing through a solution to determine the concentration of constituent species in the solution. This absorption process is caused by the same mechanism as atomic absorption or atomic emission, with the exception that the energy imparted by the electromagnetic radiation is causing molecular orbital transitions as opposed to atomic orbital transitions. In atomic spectroscopy the emission line or absorption line is very narrow, but the molecular absorption spectra exhibit relatively broad bands due to vibrational broadening.

When metals react with reagents under appropriate conditions, they will form light-absorbing, colored compounds. The amount of light absorbed by these compounds can be directly related to the concentration of the metal when compared to known standards. Thus methods can be engineered for quantitative determinations of metals in oil.

4.1 BASIC DESCRIPTION OF METHODOLOGY FOR OIL. Basically, the problem involved with the colorimetric determination of metals in oil can be divided into three parts. The first two parts involve the chemistry of the system; the third part the absorbance measurements and interpretation of the results.

In order to properly analyze metals in oil, all the particulate metal must be dissolved and the resulting ions must be extracted from the oil. The literature reviewed has shown that all the metals can be dissolved simultaneously using appropriate acid mixes, temperatures of solution and agitation in approximately 1 to 2 minutes. The fact that the oil and the aqueous phase containing the acids are immiscible facilitates the extraction process. Both the extraction and dissolution processes can be done simultaneously.

After the initial separation, the ions must be placed in an environment, which is conducive to color development. In the majority of procedures reviewed, the pH of the solution was critical and appropriate buffers were therefore utilized. Also, other reagents such as oxidizing or reducing compounds may be necessary to change the metal to the proper oxidation state for the reaction. The color-developing compound is the most important consideration and its proper selection allows suitable detection limits and freedom from interferences.

Finally the amount of light absorption of the colored solution is measured and compared to standards. From this information the concentration of the metals is calculated.

4.2 DETECTION LIMITS. There is an overwhelming number of procedures in colorimetry published in the literature. Each procedure offers some advantage, which distinguishes it from the rest, such as simplicity, freedom from interferences or detection range. An overall view of colorimetric procedures shows little difficulty in obtaining the desired detection limits and monitoring range.

4.3 PARTICLE SIZE. As all colorimetric procedures require the metal to be in the ionic form, dissolution of particles by acids is necessary. In the process of dissolving the particles, the particle size problems exhibited by other techniques is eliminated.

4.4 MATRIX EFFECT. No appreciable matrix effects are anticipated in a normal colorimetric determination of wear metals in oil. The only problems foreseen are cleanup operations due to the ability of oil to cling to surfaces.

4.5 RESOLUTION AND INTERFERENCES. In colorimetry the absorption bands are relatively broad. The width of the absorption band makes it impractical to make absorbance measurements of more than three color-absorbing species simultaneously in the same solution. The elements should be measured separately, and then the resolution of the spectrometer is not critical. Alternatively, for example, meaningful absorbance measurements can be made with a simple filter instrument.

The freedom from interferences is directly related to the proper selection of the developing reagent and the chemical environment of the final solution. Thus, the elimination of interferences is procedural and not instrumental.

4.6 MULTIELEMENT. As reviewed in the literature, there is no difficulty in analyzing all nine elements from an oil matrix. Furthermore, there is not an appreciable problem with interferences when the reagents and conditions are selected carefully. But, as stated in previous sections, the broad absorption bands generated in a colorimetric determination necessitates the measurement of each element separately.

Fortunately, due to the lack of the requirement for spectral resolution, the spectrophotometer is small and it is feasible to consider using more than one spectrophotometer so that the elements could be analyzed simultaneously.

4.7 PORTABILITY. An instrument using the colorimetry technique would easily meet the size and weight requirements for portability. The problem with portability, however, pertains to the environmental requirements outlined in the Statement of Work and with the handling of the chemicals used. The reagents used to develop color are susceptible to degradation under extreme temperature fluctuations. The pH of the buffers will change with temperature so that the accuracy of the measurement will change. As with any "wet chemical" procedure, there are a certain number of chemicals to be handled, which include concentrated acids - thus making the disposal of used solutions critical.

4.8 TIME OF ANALYSIS. The time required to perform an analysis of wear metals in oil is also critical. In order to minimize the time required to analyze the metals, a series of spectrophotometers could be used to measure the absorbance of the final colorimetric solutions simultaneously. Another approach would be a spectrophotometer with several sample compartments that are each analyzed sequentially under microprocessor control.

The problem ultimately lies in the time for preparing the sample solutions. If all five elements are to be prepared separately, the total time of the analysis would be over one hour. Thus it is necessary to design a system for simultaneously processing all the metals in the oil sample. This system would involve a method for dissolving, extracting and developing the color; then the results would be read for all the elements at the same time.

Figure A-3 proposes a system that would greatly expedite this processing of the oil sample. A "best" case and "worst" case analysis time for the system, or, for that matter, any similar system, yields an estimated time of 15 minutes for analysis of the "must" elements.

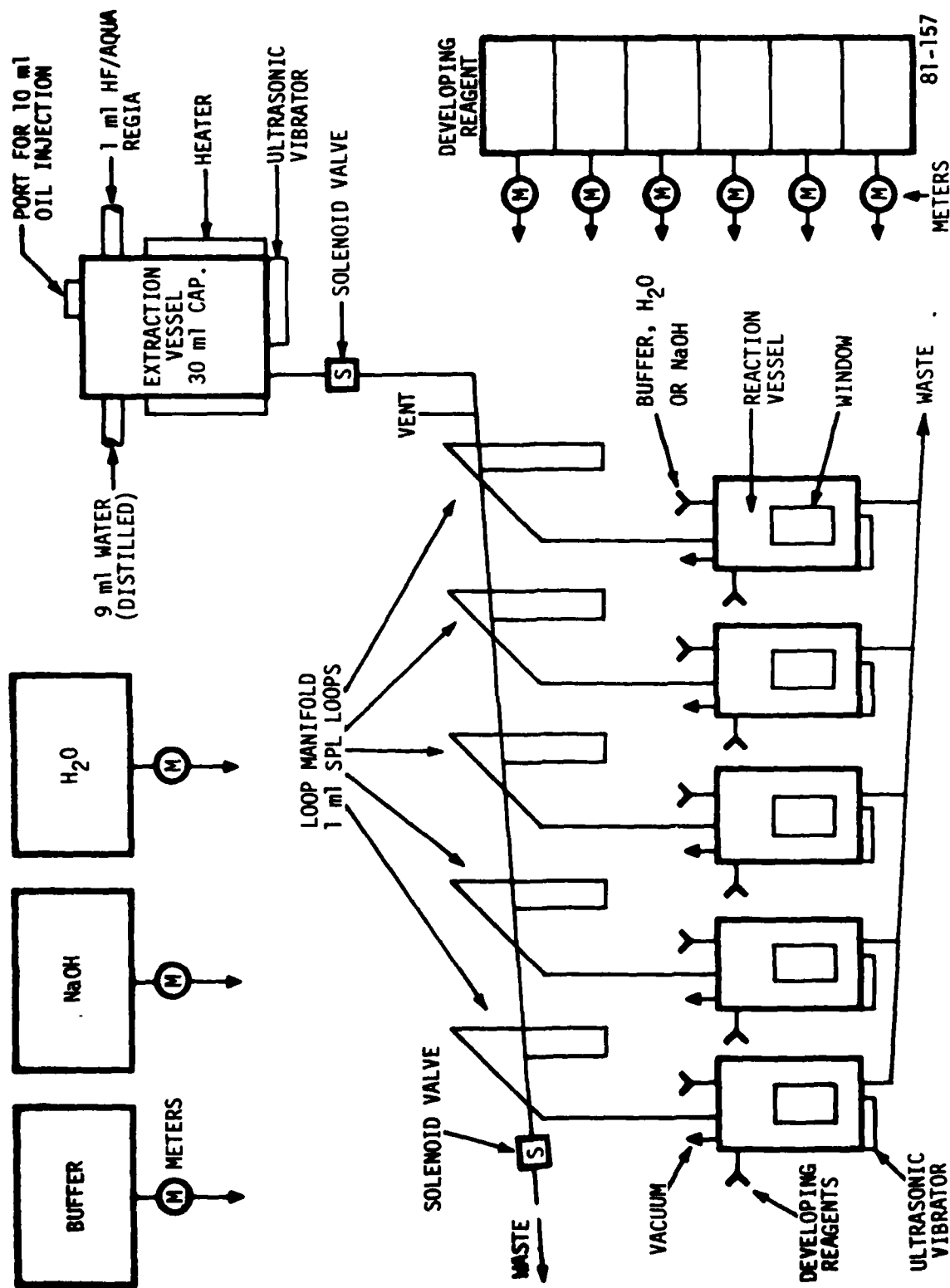


Figure A-3. Schematic Diagram for a Colorimetric Configuration

APPENDIX B
DATA MATRICES

TABLE B-1. DATA MATRIX

Rotating Disc Electrode - AES									
TECHNIQUE									
Good		Moderate		None		None			
MULTIELEMENT		MATRIX EFFECTS		SAMPLE PREP.		GASES			
Low/Moderate		Good		Low/Medium		Moderate			
PART. SIZE DEPEND.		SUIT. FOR TRI-SERVICES STD.		POWER CONSUMPTION		SUIT. FOR FIELD			
Low/Moderate		Good		Good		< 5 Min			
PART. SIZE DEPEND.		SUIT. FOR 110/220 V		ANALYSIS TIME					
ELEMENT	DETECTION LIMITS		ESTIMATED PRECISION		TECHNIQUE		OVERALL		
	UPPER (a)	LOWER (a)	UPPER	LOWER	DETECTABILITY	FUNCTIONALITY	REPEATABILITY	SUITABILITY	AND COMMENTS
Fe	500	0.2	4.1	NR	Good	Good	Good	Good	Good
Ti	100	0.1	4.7	NR	Good	Good	Good	Good	Good
Ag	20	0.02	6.0	NR	Good	Good	Good	Good	Good
Cr	100	0.1	3.1	18	Good	Good	Fair	Good	Good
Al	200	0.1	8.5	3.6	Good	Good	Good	Good	Good
Si	500	1.0	3.9	43	Good	Good	Poor	Fair	Fair
Mg	1.0	0.005	3.3	NR	Good	Good	Good	Good	Good
Ni	100	0.3	2.7	NR	Good	Good	Good	Good	Good
Cu	200	0.05	1.9	NR	Good	Good	Good	Good	Good

(a) Detection limits are specific for wear metals in oil.

(b) The precision is estimated at the upper and lower monitoring range.

NOTE: NR. indicates that the information was not recorded in the literature that was reviewed.

TABLE B-1 (continued)

Graphite Furnace - Atomic Emission TECHNIQUE		None SAMPLE PREP.		Argon (1 l./min) GASES	
Good MULTIELEMENT		Major MATRIX EFFECTS		Medium POWER CONSUMPTION	
Low for < 15 PART. SIZE DEPEND.		Good SUIT. FOR TRI-SERVICES STD.		Good SUIT. FOR 110/220 V	
ELEMENT	DETECTION LIMITS PPM		ESTIMATED PRECISION (RSD) % (c)		OVERALL SUITABILITY AND CONTENTS
	UPPER (b)	LOWER (a)	UPPER	LOWER	
Fe	2.0	0.017	NR	4.3	Poor (a)
Tl	1.0	0.010	NR	3.9	Poor (a)
Ag	0.04	0.0004	NR	NR	Poor (a)
Cr	0.04	0.0004	NR	5.3	Poor (a)
Al	0.004	0.00004	NR	7.4	Poor (a)
Si	8.8	0.088	NR	3	Poor (a)
Mg	0.2	0.002	NR	NR	Poor (a)
Ni	0.4	0.004	NR	3.8	Poor (a)
Cu	0.2	0.002	NR	5	Poor (a)

(a) No linearity or very poor linearity observed in the calibration curves for some of the elements.

(b) From the literature, the upper detection limit is two orders of magnitude above the lowest detection limit.

(c) The precision is estimated at the upper and lower monitoring range.

Note: NR indicates that the information was not recorded in the literature that was reviewed.

TABLE B-1 (continued)

DCP - Atomic Emission TECHNIQUE				Dilution SAMPLE PREP.		Argon 10 l/Min GASES	
Good MULTIELEMENT		Minor MATRIX EFFECTS		Moderate POWER CONSUMPTION		Moderate SUIT. FOR FIELD	
Moderate PART. SIZE DEPEND.		Good SUIT. FOR TRI-SERVICES STD.		Good SUIT. FOR 110/220 V		< 5 Min ANALYSIS TIME	
ELEMENT	DETECTION LIMITS (b) PPM		ESTIMATED PRECISION (RSD)% (c)		TECHNIQUE FUNCTIONALITY DETECTABILITY/REPEATABILITY	OVERALL SUITABILITY AND COMMENTS	
	UPPER (a)	LOWER (a)	UPPER	LOWER			
Fe	2000	0.020	1.7	0.9	Good	Good	
Tl	2600	0.026	1.4	4.7	Good	Good	
Ag	2600	0.026	0.9	2.6	Good	Good	
Cr	2000	0.020	1.3	2.7	Good	Good	
Al	3200	0.032	1.7	2.7	Good	Good	
Si	4200	0.042	9.5	3.1	Good	Fair	
Mg	3200	0.032	1.6	2.9	Good	Good	
Ni	8000	0.080	2.4	2.6	Good	Good	
Cu	2200	0.022	1.1	1.8	Good	Good	

(a) Detection limits are specific for metals in oil.

(b) From the literature the upper detection limit is 5 orders of magnitude above the minimum detection limit.

(c) The precision is estimated at the upper and lower monitoring range.

TABLE B-1 (continued)

ICP - Atomic Emission		Dilution		Argon 7 l/Min	
TECHNIQUE		SAMPLE PREP.		GASES	
ELEMENT	DETECTION LIMITS (b) PPM	ESTIMATED PRECISION (RSD) % (c)		TECHNIQUE FUNCTIONALITY	OVERALL SUITABILITY AND COMMENTS
		UPPER	LOWER		
Fe	4000	(a) 2.8	(a) 2.7	Good	Good
Ti	3000	(a) 1.3	(a) 4.0	Good	Good
Ag	2000	(a) 2.2	(a) 5.7	Good	Good
Cr	3000	(a) 3.8	(a) 8.3	Good	Good
Al	9000	(a) 4.9	(a) 32.5	Fair	Good
Si	7000	1.9	NR	Good	Good
Mg	700	(a) 2.8	(a) 5.4	Good	Good
Ni	10,000	7	(a) 1.6	Good	Good
Cu	600	(a) 0.8	(a) 7.3	Good	Good

(a) Detection limits are specific for metals in oil.

(b) From the literature the upper detection limit is 5 orders of magnitude above the minimum detection limit.

(c) The precision is estimated at the upper and lower monitoring range.

Note: NR indicates that the information was not recorded in the literature that was reviewed.

TABLE B-1 (continued)

Flame Atomic Absorption TECHNIQUE			Dilution SAMPLE PREP.		Nitrous Oxide + Acetylene GASES	
ELEMENT	DETECTION LIMITS (b) PPM		ESTIMATED PRECISION (RSD)% (c)		TECHNIQUE FUNCTIONALITY	
	UPPER (a)	LOWER (a)	UPPER	LOWER	DETECTABILITY	REPEATABILITY
Fe	50	0.004	0.1	3	Good	Good
Ti	430	0.1	0.1	3	Good	Good
Ag	20	0.001	NR	14	Good	Fair
Cr	100	0.005	1.9	6	Good	Good
Al	300	0.1	0.1	2	Good	Good
Si	430	4.0	NR	NR	Poor	Poor
Mg	10	0.0003	0.1	12	Good	Fair
Mn	25	0.005	NR	0.4	Good	Good
Cu	50	0.004	1.9	1.6	Good	Good

(a) Lowest detectable limit is the concentration needed to generate a S/N ratio of two.
 (b) Upper detectable limit is estimated from sensitivity data or extracted from the literature.
 (c) The precision is estimated at the upper and lower monitoring range.

TABLE B-1 (continued)

Graphite Furnace Atomic Absorption		None		Argon (1 l/Min)	
TECHNIQUE		SAMPLE PREP.		GASES	
MULTIELEMENT	Good	Moderate	Medium	Good	
	MATRIX EFFECTS		POWER CONSUMPTION	SUIT. FOR FIELD	
PART. SIZE DEPEND.		SUIT. FOR TRI-SERVICES STD.		< 5 Min	
Low for		Good		SUIT. FOR 110/220 V	
ELEMENT	DETECTION LIMITS (b) PPM		ESTIMATED PRECISION (RSD)% (a)		OVERALL SUITABILITY AND COMMENTS
	UPPER (a)	LOWER (a)	UPPER	LOWER	
Fe	2.5	5×10^{-5}	3	6	Good
Ti	100	2×10^{-3}	2	7	Good
Ag	0.25	5×10^{-6}	11	12	Good
Cr	0.5	1×10^{-4}	4	7	Good
Al	2.5	5×10^{-5}	2	4	Good
Si	0.15	2.5×10^{-6}	4	7	Good
Mg	0.10	2.0×10^{-6}	4	7	Good
Ni	0.25	4.5×10^{-4}	5	8	Good
Cu	1.5	3.0×10^{-5}	2	13	Fair

(a) Detection limits are based on a 20 μ l sample volume.(b) Values were extracted from the literature and adjusted for 20 μ l sample volume.

(c) The precision is estimated at the upper and lower monitoring range.

Note: No distinction is made between graphite tubes, rods, braids or filaments.

TABLE B-1 (continued)

ICP - Atomic Absorption		Dilution		Argon 10 l/Min	
TECHNIQUE		SAMPLE PREP.		CASES	
Good	Minor	High		Poor	
	MATRIX EFFECTS	POWER CONSUMPTION		SUIT. FOR FIELD	
High	Moderate	Good		< 5 Min	
	SUIT. FOR TRI-SERVICES STD.	SUIT. FOR 110/220 V		ANALYSIS TIME	
PART. SIZE DEPEND.					

ELEMENT	DETECTION LIMITS		ESTIMATED PRECISION		TECHNIQUE		OVERALL SUITABILITY AND COMMENTS
	UPPER	LOWER (c)	UPPER	LOWER	DETECTABILITY	REPEATABILITY	
Fe	200	2.0 (b)	No Precision Information found in the Literature		Poor	Poor	Poor
Tl	250	5.0			Poor	Poor	Poor
Ag	75	0.5			Fair	Poor	Poor
Cr	100	2.0 (b)			Poor	Poor	Poor
Al	200	0.0			Not Acceptable	Not Acceptable	Not Acceptable
Si	(a)	> 100			Not Acceptable	Not Acceptable	Not Acceptable
Mg	3	0.06			Good	Good	Good
Ni	100	2.0 (b)			Poor	Poor	Poor
Cu	140	1.5			Poor	Poor	Poor

(a) No available information in the literature.

(b) Estimated using the relative sensitivities of these elements in a flame with an element investigated in an ICP - Atomizer.

(c) Estimated by extrapolating the sensitivity to 50% absorption.

TABLE B-1 (continued)

X-Ray Spectroscopy-Wavelength Dispersive		TECHNIQUE		None		None	
				SAMPLE PREP.		GASES	
Good		Minor		Moderate		Good	
MULTIELEMENT		MATRIX EFFECTS		POWER CONSUMPTION		SUIT. FOR FIELD	
Moderate		Good		Good		< 5 Min	
PART. SIZE DEPEND.		SUIT. FOR TRI-SERVICES STD.		SUIT. FOR 110/220 V		ANALYSIS TIME	

ELEMENT	DETECTION LIMITS PPM		ESTIMATED PRECISION (RSD)%		TECHNIQUE FUNCTIONALITY		OVERALL SUITABILITY AND COMMENTS
	UPPER (a)	LOWER (a)	UPPER	LOWER	DETECTABILITY	REPEATABILITY	
Fe	Percent	2 ppm	(e)	(e)	Fair	NR	Poor
Ti	Percent	8 ppm	(e)	(e)	Poor	NR	Poor
Ag	Percent	5 ppm	(e)	(e)	Poor	NR	Poor
Cr	Percent	6 ppm	(e)	(e)	Poor	NR	Poor
Al	Percent	3 ppm	(e)	(e)	Poor	NR	Poor
Si	Percent	7 ppm	(e)	(e)	Poor	NR	Poor
Mg	Percent	12 ppm	(e)	(e)	Poor	NR	Poor
Ni	Percent	4 ppm	(e)	(e)	Poor	NR	Poor
Cu	Percent	4 ppm	(e)	(e)	Poor	NR	Poor

(a) Estimated directly from literature.

(b) Detected in a steel matrix, 40 second analysis time.

(c) Detected in a aluminum matrix, 40 second analysis time.

(d) Detected in a sand matrix, 40 second analysis time.

Note: NR indicates that the information was not recorded in the literature that was reviewed.

(e) Precisions are approximately 1% at nominal concentration ranges.

TABLE B-1 (continued)

X-Ray Spectroscopy-Energy Dispersive		TECHNIQUE		None		None	
Good (Z > 22)		Minor		Moderate		Good	
MULTIELEMENT		MATRIX EFFECTS		POWER CONSUMPTION		SUIT. FOR FIELD	
Moderate		Good		Good		< 5 Min	
PART. SIZE DEPEND.		SUIT. FOR TRI-SERVICES STD.		SUIT. FOR 110/220 V		ANALYSIS TIME	

ELEMENT	DETECTION LIMITS PPM		ESTIMATED PRECISION (RSD)% (b)		TECHNIQUE FUNCTIONALITY		OVERALL SUITABILITY AND COMMENTS
	UPPER (a)	LOWER (a)	UPPER	LOWER	DETECTABILITY	REPEATABILITY	
Fe	Percent	0.7 ppm	(b)	(b)	Fair	NR	Fair
Ti	Percent	1.0 ppm	(b)	(b)	Poor	NR	Poor
Ag	Percent	1.0 ppm	(b)	(b)	Poor	NR	Poor
Cr	Percent	0.8 ppm	(b)	(b)	Fair	NR	Fair
Al	Percent	> 10 ppm	(b)	(b)	Not Acceptable	NR	Not Acceptable
Si	Percent	> 10 ppm	(b)	(b)	Not Acceptable	NR	Not Acceptable
Mg	Percent	> 10 ppm	(b)	(b)	Not Acceptable	NR	Not Acceptable
Ni	Percent	0.7 ppm	(b)	(b)	Fair	NR	Fair
Cu	Percent	0.7 ppm	(b)	(b)	Fair	NR	Fair

(a) Specific for metals in oil, 100 sec counting time.

(b) Better than 1% at 1000 ppm level (best precision between 0.1 and 1% conc.)

Note: NR indicates that the information was not recorded in the literature that was reviewed.

TABLE B-1 (continued)

Colorimetry TECHNIQUE		(a) SAMPLE PREP.		None GASES	
ELEMENT	DETECTION LIMITS PPM	NAME OF COLORIMETRY REAGENT	TECHNIQUE FUNCTIONALITY DETECTABILITY/REPEATABILITY	OVERALL SUITABILITY AND COMMENTS	
Fe	1.2	Bathophenanthroline	Good	Good	
Ti	2.8	Several	Good	Good	
Ag	1.0	4,4' Bis (Dimethyl Amino)-Thiobenzophenone	Good	Good	
Cr	0.5	Alizarin III	Good	Good	
Al	4	Dimethylglyoxime + Bromine Water	Good	Good	
Si	2	1,5 Diphenyl Hydrozide	Good	Good	
Mg	5	Heteropoly Blue	Good	Good	
Ni	1.2	AHDCAS	Good	Good	
Cu	3	Bicinchominate	Good	Good	

(a) Sample must be diluted; the metals must be dissolved with acid; the appropriate buffers must be added; the necessary colorimetric reagent must be added.

Note 1: The sample solution can be diluted to obtain appropriate monitoring range.

Note 2: No precision information was recorded in the literature reviewed.

Note 3: Listed colorimetric reagents are only a sample of reagents that would work.

APPENDIX C

RADIATION LEVEL CALCULATION FOR RADIOACTIVE TAGGING TECHNIQUES

Let us assume that we irradiate the bearings in a B-52 engine and determine the subsequent wear metal in the lubricating oil. A reasonable minimum detectable net counting rate is 60 counts/minute with an average counting efficiency of 20 percent. The minimum disintegration rate needed is therefore 300 disintegrations per minute (dpm). As 1 curie = 2.2×10^{12} dpm, the minimum activity needed in the oil sample is 1.4×10^{-10} curie.

Assume the oil volume in the B-52 is 120 liters (l) and the sample size for wear measurement is 10 milliliters (ml).

$$\begin{aligned} \text{Minimum total activity in oil} &= \frac{120 \times 10^3 \text{ ml}}{10 \text{ ml}} \times 1.4 \times 10^{-10} \text{ curie} \\ &= 1.7 \times 10^{-6} \text{ curie} \end{aligned}$$

For wear metal measurement, this minimum activity should be equal to or less than 1 ppm. We will assume that the wear metal concentration in the oil reaches 1000 ppm, when the bearing wear is 1 percent of its original weight.

Then, minimum total activity needed in bearing for adequate measurement of wear =

$$\begin{aligned} &\frac{1.7 \times 10^{-6} \text{ curie} \times 1000}{0.01} \\ &= 1.7 \times 10^{-1} \text{ curie} \end{aligned}$$

Assume the half-life is 2.5 years and the expected useful life for this irradiated part is 10 years.

Then $N_0 = 16N$ where N_0 = initial activity

N = activity after 10 years.

$$\begin{aligned} \text{Original total activity needed in bearing} &= 1.7 \times 10^{-1} \text{ curie} \times 16 \\ &= 2.7 \text{ curie} \end{aligned}$$

Assume the average γ radiation energy is 300 keV and that the bearing is a point source γ emitter. Then -

$$D\gamma = 0.54 A E n \quad \text{where } D\gamma = \text{exposure dose at 1 meter (R/hr)}$$

A = source activity (curie)

E = energy per quantum (meV)

n = number of quanta per disintegration

$$D\gamma = 0.54 \times 2.7 \times 0.3 \times 1$$

$$= 0.44 \text{ Roentgen/hr.}$$

This calculation is for one element. For five elements the total exposure dose at one meter away from the parts would be 2.2 Roentgen/hr., compared with the safe exposure level of 0.1 Roentgen/week.

Although the assumptions in this calculation are approximations, the calculation still shows that the order of magnitude of the radiation level would be hazardous for maintenance personnel.

APPENDIX D. General Comparison of the Ten Techniques

Requirement Technique	Multi- Element	Particle Size Dependence	Matrix Effect	Tri-Serv Standard Suitability	Sample Preparation	Power Consumption	110/220 V Suitability	Gases Needed	Analysis Time (Mins)	Repeat- ability	Detect- ability
Flame AA	Moderate	High	Minor	Good	Yes	Low	Yes	High	< 5	Good	Good
Graphite Furnace AA	Moderate	Low	Minor	Good	No	Moderate	Yes	Low	< 5	Good	Good
ICP AA	Moderate	Moderate	Minor	Moderate	Yes	High	Yes	High	< 5	Poor	Poor
Graphite Tube AES	Good	Low	High	Good	No	Moderate	Yes	Low	< 5	Poor	Good
ICP AES	Good	Moderate	Minor	Good	Yes	High	Yes	High	< 5	Good	Good
DCP AES	Good	Moderate	Minor	Good	Yes	Moderate	Yes	High	< 5	Good	Good
Electrode AES	Good	Low	Minor	Moderate	No	Moderate	Yes	None	< 5	Good	Good
Colorimetry	Good	Low	Minor	Good	Yes	Low	Yes	None	> 15	Good	Good
X-Ray Wavelength	Moderate	Moderate	Minor	Good	No	Moderate	Yes	None	< 5	Poor	Poor
X-Ray Energy Des	Moderate	Moderate	Minor	Good	No	Moderate	Yes	None	< 5	Poor	Poor
Radioactive Tagging	Poor	Low	None	Poor	No	Low	Yes	None	< 5	Good	Good

APPENDIX E

EVALUATION OF PRECONCENTRATION OF WEAR METALS FOR X-RAY FLUORESCENCE ANALYSIS: FILTER CLOGGING

The filtration system consists of two 0.5 inch diameter filters in tandem. The first filter, of one μm pore size, is used to remove the large particles; the second filter, of 0.1 μm pore size, is the filter used to collect the metals for subsequent X-ray analysis.

The best case evaluation of the system is for particles that are microspheres approaching 1 μm in diameter. Thus, the particle will pass through the first filter and evenly coat the surface area of the second filter.

Conditions: 5 mL of oil through filter; the filter is 1/2 inch in diameter - the area is 1.27 cm^2 .

Assume: Average density is that of iron, 7.8 g/cm^3 ; the filter is coated with one layer before it blocks.

Total number of particles (N) = Area of filter/Projected area of particle

$$N = 4 \times 1.27 \text{ cm}^2 / \pi D^2 \quad D = \text{diameter of particle (cm)}$$

$$\text{Total volume of all particles} = \frac{4 \times 1.27}{\pi D^2} \times \frac{1}{6} \pi D^3 = 0.847 D$$

$$\text{Total weight of all particles} = 0.847 D \times 7.8 \text{ g/cm}^3$$

Converting diameter to μm and weight to milligrams yields:

$$\text{mg} = 0.661 d \quad d = \text{diameter of particle } (\mu\text{m})$$

If 5 mL of sample is used then the concentration of particulates, in ppm is:

$$\frac{0.661 d}{5 \text{ mL}} \times \frac{1000 \text{ mL}}{L} = \frac{\text{mg}}{L} = \text{ppm} = 132 d$$

	0.1 μ	0.3 μ	0.6 μ	1.0 μ
Concentration in ppm to completely coat the filter	13	40	80	132

The total number of suspended particles includes all particulate matter, some of which will be non-metallic particles. As the oil contains a distribution of particle sizes, it is estimated that between 10 and 220 ppm of suspended particles will cause blockage of the filter.

APPENDIX F

BASIC LIMITING FACTORS TO FACILITATE A SIZE EVALUATION FOR OPTICAL SPECTROMETERS

1. ATOMIC EMISSION SPECTROSCOPY. After a careful analysis of the spectral data in the Massachusetts Institute of Technology wavelength tables and supplemental literature, the maximum bandpass estimated for the polychromator in a field instrument is 0.5 Å. This value resulted from a best case analysis, disregarding physical effects and assuming the instrument can be fine tuned to allow complete isolation of the desired spectral line.

At this point we can state basic optical components which are commercially available and are the best components for doing the job of minimizing monochromator size. These are:

- a. 5 cm x 5 cm 3600 groove/mm grating
- b. 35 micron (.035 mm) entrance and exit slits

1.1 LINEAR DISPERSION AND PLATE FACTOR NEEDED

$$0.5 \text{ Å}/0.035 \text{ mm} = 14 \text{ Å/mm (plate factor)}$$

$$\text{which equals } .071 \text{ mm/Å (linear dispersion)} = d\ell/d\lambda$$

1.2 FOCAL LENGTH OF INSTRUMENT

Using the equation for equating linear dispersion to angular dispersion, we have.

$$\frac{d\ell}{d\lambda} = \frac{Rn}{d \cos \beta}$$

R = focal length

$$d = \text{Å/groove}$$

$$= \frac{10^7}{3600} = \frac{2778 \text{ Å}}{\text{groove}}$$

$$n = \text{order} = 1$$

Also, assuming we are operating close to the grating normal where $\beta = 0$ and $\cos \beta = 1$. Here the wavelengths disperse in a linear fashion for quite a range. Thus

$$.071 \text{ mm/Å} \times \frac{2778 \text{ Å}}{\text{groove}} = 198 \text{ mm} = 20 \text{ cm focal length}$$

1.3 PLATE LENGTH

- a. All nine elements (spectral range = 1140 Å)

$$1140 \text{ Å} / 14 \text{ Å/mm} = 81.4 \text{ mm} = 8.14 \text{ cm} \\ (3.3 \text{ inch})$$

- b. Five "Must" Elements (spectral range = 590 Å)

$$590 \text{ Å} / 14 \text{ Å/mm} = 42.1 \text{ mm} = 4.21 \text{ cm} \\ (1.66 \text{ inch})$$

1.4 THERORETICAL RESOLUTION

Equation: $R = nN = \frac{\lambda}{\Delta\lambda}$

$n = \text{Order} = 1$

$N = \text{Total \# of grooves } 50 \text{ mm} \times 3600 \text{ g/mm}$
 $= 180,000$

$\lambda = 3500 \text{ Å}$ (taken at the midpoint of the
desired spectral range)

RESOLUTUION = $1 \times 180,000$

$$\frac{\lambda}{\Delta\lambda} = 180,000$$

$\Delta\lambda = .02 \text{ Å}$ for complete resolution

2. ATOMIC ABSORPTION SPECTROSCOPY. Estimated from the comparison tables for atomic absorption wavelengths, the appropriate polychromator should have a bandpass of 10 Å. We already have seen that a 20 cm focal length polychromator will yield a maximum bandpass of 0.5 Å with a 0.035 mm exit slit. The wider the exit slit compared to a narrow spectral line width the more stable the polychromator for field use. Thus the maximum exit slit width is determined which still retains a 10 Å bandpass.

Grating: 5 x 5 cm, 3600 groove/mm grating

$$3600 \text{ grooves/mm} = 2778 \text{ Å/groove}$$

Thus:

- a. Linear Dispersion

$$\frac{200 \text{ mm} \times 1}{2778 \text{ Å} \times 1} = 0.071 \frac{\text{mm}}{\text{Å}}$$

- b. Plate Factor $1/.071$ $= 14.1 \text{ Å/mm}$
- c. Bandpass 10 Å estimated from tables
- d. Slit Width $10 \text{ Å}/14.1 \text{ Å/mm} = 0.71 \text{ mm}$
- e. Resolution $R = nN = \lambda/\Delta\lambda$

3000 Å (midpoint of desired spectral range)

$$N = 3600 \times 50 \text{ mm} = 180,000$$

$$\frac{3000}{180,000} = \Delta\lambda = .02 \text{ Å}$$

- f. Plate Length

$$3800 \text{ Å to } 2200 \text{ Å} \quad \Delta\lambda = 1600 \text{ Å}$$

free spectral range

Plate Length

$$1600 \text{ Å}/14.1 \text{ Å/mm} = 113 \text{ mm}$$

$$= 11.3 \text{ cm} = 4.5 \text{ inches}$$

3. CONCLUSION. Conceivably, a small emission spectrometer could be designed which would have adequate resolution, bandpass and dispersion for portability. Yet the problem of spectral alignment and stability is still severe. The practical case of line broadening and aberration are also present and with instruments of short focal lengths the discrepancies may be serious.

Atomic absorption using a polychromator is feasible with regard to size and stability as long as light source interferences are minimal.

APPENDIX G

THEORETICAL DETERMINATION OF SETTLING RATES VS PARTICLE SIZE AND VISCOSITY OF OIL

Following Stoke's law and assuming spherical particles with a density of 7.86 g/cm³ (IRON) and a density of oil of 0.80 g/cm³.

$$1) \quad \frac{4}{3} \pi r^3 (P - P_o)g = 6\pi\eta rV \quad r = \text{Radius of particle (cm)}$$

P = Density of particle

Rearrange and combine terms P_o = Density of oil

$$2) \quad 1556 \frac{r^2}{\eta} = V \quad g = 1000 \text{ cm/sec}^2$$

$$r^2 = \frac{D^2}{4} \quad \text{Thus} \quad \eta = \text{Viscosity (Poise)}$$

V = Settling rate (cm/sec)

$$3) \quad 389 \frac{D^2}{\eta} = V \quad D = \text{Diameter of particle (cm)}$$

Convert to d = microns, η = Centipoise and V = mm/min.

Yields

d = diameter of particle microns

$$389 \frac{\text{poise}}{\text{cm-sec}} \times 10^{-8} \frac{\text{cm}^2}{\text{microns}^2} \times 100 \frac{\text{centipoise}}{\text{poise}} \times \frac{60 \text{ sec}}{\text{min}}$$

$$\times 10 \frac{\text{mm}}{\text{cm}} \times \frac{d^2}{\eta} = \gamma \quad \eta = \text{Centipoise}$$

$$\frac{.233 d^2}{\eta} = \gamma \quad \gamma = \text{Settle rate mm/min.}$$

Particles will not settle at this rate continuously, but rather, will start at rest and accelerate by the influence of gravity until this speed is reached (asymptotically). Thus this settling rate represents the fastest value attainable.

TABLE G-1. SETTLING RATE IN MILLIMETERS PER MINUTE FOR VARIOUS PARTICLE SIZES AT 1, 10, 100 AND 1000 CENTIPOISE OIL VISCOSITY

Viscosity Particle Size	1 CPS	10 CPS	100 CPS	1000 CPS
1	0.23	0.02	0.002	--
5	5.83	0.58	0.06	0.006
10	23.3	2.33	0.23	0.023
12	33.6	3.36	0.34	0.034
15	52.4	5.24	0.52	0.052
18	75.5	7.55	0.76	0.076
20	93.2	9.32	0.93	0.093
25	146.0	14.6	1.5	0.15
30	210.0	21.0	2.1	0.21
35	285.0	28.5	2.9	0.29
40	373.0	37.3	3.7	0.31
45	472.0	47.2	4.7	0.47
50	583.0	58.3	5.8	0.58

$$\text{Kinematic Viscosity (Centistokes, CS)} = \frac{\text{Centipoise @ 20°C}}{\text{Density}}$$

APPENDIX H

EFFECT OF PARTICLE SIZE ON PARTS PER MILLION (PPM) LIMITS AND PRECISION IN FURNACE ATOMIC ABSORPTION SPECTROSCOPY

The system consists of some means of pipetting a 20 microliter volume of oil into the graphite furnace atomizer of an atomic absorption spectrometer. Assume that the particles are microspheres with the density of iron (7.86 g/cc).

1. CONCENTRATION IN PPM FOR ONE PARTICLE AS A FUNCTION OF PARTICLE SIZE. 20 microliter sample of oil.

$$\text{ppm} = \frac{4}{3} \pi r^3 10^{-12} \text{ cm}^3 \cdot 7.86 \text{ g/cm}^3 \cdot \frac{1000}{20 \mu\text{l}} \mu\text{l/ml} \cdot 10^6 \frac{\mu\text{g}}{\text{g}}$$

$$\begin{aligned} \text{ppm} &= 1.65 \times 10^{-3} \cdot r^3 & r &= \text{microns} \\ &= 2.1 \times 10^{-4} \cdot d^3 & d &= \text{diameter of particle in microns} \end{aligned}$$

TABLE H-1. CONCENTRATION (PPM) FOR ONE PARTICLE IN 20
MICROLITER SAMPLE AS A FUNCTION OF PARTICLE SIZE

Particle Size (μm)	0.01	0.1	1	2.5	5	10	25
Concentration ppm	2.1×10^{-10} ppm	2.1×10^{-7} ppm	2.1×10^{-4} ppm	3.3×10^{-3} ppm	2.6×10^{-2} ppm	0.21 ppm	3.3 ppm

2. NUMBER OF PARTICLES TO GENERATE 1, 10, AND 100 PPM METAL IN OIL AS A FUNCTION OF PARTICLE SIZE. 20 microliters sample.

$$\begin{aligned} 2.1 \times 10^{-4} \cdot d^3 &= \text{ppm} & \text{For 1 particle (from 1 above)} \\ (2.1 \times 10^{-4} \cdot d^3) N &= \text{ppm} & N = \text{Number of particles} \end{aligned}$$

$$N = \frac{\text{ppm} \cdot 10^4}{2.1 d^3} = \frac{4762 \cdot \text{ppm}}{d^3}$$

3. ESTIMATION OF PARTICLE SIZE BASED ON THE RELATIVE STANDARD DEVIATION.

Assuming the overall error is due mainly to the differences in the number of particles with each sampling and assuming that the fluctuations in the total number of particles is approximated by a Poisson distribution, then:

$$\text{Standard Deviation} = \sqrt{N}$$

N = Total number of particles

$$\text{Relative Standard Deviation} = \frac{\sqrt{N}}{N} \times 100\%$$

For 0.5 μ m and 5 μ m particles at a 10 ppm level:

Particle Size	N	Standard Deviation	Relative Standard Deviation	Deviation at 10 ppm
.5 μ	3.8×10^5	620	0.2%	10 \pm 0.02 ppm
5 μ	3.8×10^2	19	5.1%	10 \pm 0.5 ppm

LIST OF ABBREVIATIONS, ACRONYMS AND SYMBOLS

1.	Å	Angstrom
2.	AAS	Atomic Absorption Spectroscopy
3.	AES	Atomic Emission Spectroscopy
4.	Ag	Silver
5.	Al	Aluminum
6.	Ar	Argon
7.	ASOAP	Army Spectroscopic Oil Analysis Program
8.	C ₂ H ₂	Acetylene
9.	Cr	Chromium
10.	Cu	Copper
11.	DCP	Direct Current Plasma
12.	DOD	Department of Defense
13.	Fe	Iron
14.	HCl	Hydrochloric Acid
15.	HF	Hydrofluoric Acid
16.	HNO ₃	Nitric Acid
17.	ICP	Inductively Coupled Plasma
18.	JOAP	Joint Oil Analysis Program
19.	Li	Lithium
20.	MIBK	Methyl-Isobutyl Ketone
21.	Mg	Magnesium
22.	Na	Sodium
23.	NASA	National Aeronautic Space Administration
24.	Ni	Nickel
25.	N ₂ O	Nitrous Oxide
26.	NOAP	Naval Oil Analysis Program
27.	PPB	Parts per Billion
28.	PPM	Parts Per Million
29.	Si	Silicon
30.	SOAP	Spectroscopic Oil Analysis Program
31.	Ti	Titanium
32.	XRFS	X-ray Fluorescence Spectroscopy
33.	W	Tungsten
34.	Zr	Zirconium

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-8